

The Conductivity and Viscosity of Solutions of Certain Salts in Mixtures of Acetone with Methyl Alcohol, with Ethyl Alcohol and Water.



By Harry C. Jones and Eugene C. Bingham.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN SALTS IN MIXTURES OF ACETONE WITH METHYL ALCOHOL, WITH ETHYL ALCOHOL AND WATER.

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PART I.

HISTORICAL REVIEW.

(a) *Conductivity and Viscosity*.—That viscosity and conductivity are related is by no means a new idea. As early as 1856, G. Wiedemann¹ studied aqueous solutions of copper sulphate and concluded that the conductivity of a solution is directly proportional to the concentration and inversely proportional to the viscosity. When formulated this would be :

$$\frac{K\eta}{\phi} = \text{constant},$$

where K is the conductivity of the solution of concentration, ϕ and η the viscosity.

Grottrian,² in 1876, measured the conductivity and viscosity of solutions at different temperatures, but obtained indecisive results.

Stephan,³ in 1883, tried a third possibility, by using mixtures of alcohol and water as a solvent. He found the temperature coefficients of conductivity and of fluidity (the reciprocal of viscosity) very much alike. He observed a minimum in his curves and proposed the formula :

¹ Pogg. Ann., 99, 229 (1856).

² *Ibid.*, 157, 130 (1876).

³ Wied. Ann., 17, 673 (1883).

$$\frac{KH}{k\eta} = \text{constant},$$

to hold up to the minimum point, and

$$\frac{wKH}{w'k\eta} = \text{constant}$$

to hold from that point on; where K is the conductivity of the equivalent aqueous solution, k the conductivity of the mixture and H and η , the corresponding viscosities. w and w' are the per cents of water in the given aqueous mixture and in the aqueous alcoholic mixture of minimal fluidity, respectively. He believed that each ion carries with it neighboring molecules of the solvent, and that ionic friction results from the friction between these and the rest of the solvent.

Dutoit and Friderich¹ introduced the association factor and concluded that, "The values of μ_v for a given electrolyte dissolved in different solvents, are a direct function of the degree of polymerization of the solvent and an indirect function of the coefficient of viscosity of these solvents."

A fourth method of changing the fluidity was resorted to by Röntgen,² and later by Warburg and Sach,³ and more exhaustively by Cohen.⁴ They subjected the aqueous solution to high pressure. Cohen found that, at low temperatures, the viscosity is decreased by the pressure, but that above 40° the viscosity increases with the pressure. In concentrated solutions of sodium and ammonium chlorides the viscosity increases nearly proportionally to the pressure and nearly independently of the temperature. Hauser⁵ showed that, at 32°, the pressure ceased to affect the fluidity of water.

Grossman,⁶ in 1883, recalculated Grotrian's results and found that the conductivity multiplied by the viscosity gave a constant independent of the temperature, and that the temperature coefficients were the same to within 1 per cent.

¹ Bull. Soc. Chim., [3], 19, 321 (1898).

² Wied. Ann., 22, 510 (1884).

³ *Ibid.*, 22, 514 (1884).

⁴ *Ibid.*, 45, 666 (1892).

⁵ Ann. d. Physik., 5, 597 (1901).

⁶ Wied. Ann., 18, 119 (1883).

Arrhenius¹ worked with aqueous solutions, to which small amounts of non-electrolytes, such as acetone and methyl and ethyl alcohols, had been added. He pointed out an empirical relation between the conductivity and the fluidity, but he saw that these quantities are not simply dependent on each other, because the conductivities of dilute solutions of different salts are not the same. This empirical relation was further developed by Euler.²

We need only mention the work of Stringberg³ and of Holland.⁴

Völlmer⁵ investigated solutions of various salts in methyl and ethyl alcohols. He found the temperature coefficients of conductivity and fluidity to be very nearly identical.

Kohlrausch and Deguisne⁶ used a formula,

$$K_t = K_{18} [1 + \alpha (t - 18^\circ) + \beta (t - 18^\circ)^2],$$

to represent the influence of temperature on conductivity, starting from 18° as a mean temperature. Kohlrausch⁷ noted that on extrapolating this curve, aqueous solutions would reach a zero value of conductivity at about -39°, which is about the temperature where the fluidity would become zero. Bousfield and Lowry⁸ showed that the viscosity of water may be represented accurately by a formula similar to the above,

$$\eta_{18} = \eta_t [1 + \alpha (t - 18) + \beta (t - 18)^2].$$

They found that the constants α and β are the same in the two formulas, to within the limits of experimental error. They believe, however, that these formulas will not hold at low temperatures and that the zero values cannot be experimentally realized. This belief is borne out by the work of Kunz.⁹

In an exceedingly interesting paper, Kohlrausch¹⁰ proposes the view that "About every ion there moves an atmosphere of

¹ Z. physik. Chem., **9**, 487; *Ibid.*, **1**, 285 (1887).

² *Ibid.*, **35**, 536 (1898).

³ *Ibid.*, **14**, 221 (1894).

⁴ Wied. Ann., **50**, 261 (1892).

⁵ *Ibid.*, **52**, 328 (1894).

⁶ Dissertation, Strassburg, 1893.

⁷ Sitz. Berlin., (1901), 1028.

⁸ P. Roy. Soc., **71**, 42 (1902).

⁹ Compt. rend., **135**, 788 (1902).

¹⁰ P. Roy. Soc., **71**, 338 (1903).

the solvent, whose dimensions are determined by the individual characteristics of the ion. . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness. . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving univalent ion, Li."

Bousfield and Lowry¹ have gone farther and have shown that we should also expect to find an upper limit of conductivity, on account of the decrease in dissociation with rise in temperature. A maximum conductivity of this sort has been observed by Franklin and Kraus² in liquid ammonia. Potassium iodide gives a maximum in conductivity, in methyl alcohol, at 160°. ³ Noyes⁴ observed a maximum conductivity with 0.1 N potassium and sodium chlorides, in water, at 280°. The formula of Slotte⁵ for variation of fluidity,

$$\eta_0/\eta = (1 + bt)^n,$$

holds at low temperatures, so that combining this formula with that of Abegg and Seitz for decrease in dielectric constant,

$$D/D' = e^{-at},$$

Bousfield and Lowry⁶ give, as the complete formula representing the effect of temperature on conductivity,

¹ *Loc. cit.*

² *THIS JOURNAL*, **24**, 83 (1900).

³ *Physic. Rev.*, **18**, 40 (1904).

⁴ *Z. physik. Chem.*, **46**, 323 (1903). *J. Am. Chem. Soc.*, **26**, 134 (1903).

⁵ *Beibl.*, **16**, 182 (1892).

⁶ *P. Roy. Soc.*, **74**, 280 (1904).

$$\frac{K_t}{K_0} = \frac{\rho_v}{\rho_0} (1 + bt)^n e^{-at}.$$

Reference should also be made to the work of Hechler.¹

(b) *Viscosity*.—The majority of workers have confined themselves either to viscosity determinations alone, or to conductivity determinations alone. We must, therefore, consider some of these if we wish to see clearly the relations between the phenomena.

We need simply mention here the work of Poiseuille,² Noack,³ Pagliani and Battelli,⁴ Slotte,⁵ Gartenmeister⁶ and Traube.⁷ The monumental work of Thorpe and Rodger⁸ requires more attention. They worked with very great accuracy both with pure liquids⁷ and with mixtures,⁹ and over a considerable range of temperature. They have shown that the formula of Slotte gives the best results. They proved, conclusively, what had been hinted at before, that "Viscosity may be taken as the sum of the attractive forces in play between the molecules; . . . that an increment of CH₂ in chemical composition, or the substitution of an atom of Cl, Br, or I for an atom of hydrogen, brings about a definite change in the magnitude of the viscosity. It is, therefore, made evident that viscosity or intermolecular attraction is, in reality, a property of the atoms of which the molecules are composed. Isomers have nearly, but not the same viscosity, yet the effect of CH₂ is the same as in the normal compounds. The effects due to ring grouping, iso- and double-linkages, and changes in the condition of the oxygen may be quantitatively allowed for. . . . But water and the alcohols show no agreement with the calculated values."

Hydrogen is calculated to have an effect on molecular viscosity of 44.5, carbon of 31 and iso-linkage, for example, of

¹ Dissertation, Münster (1904).

² Mem. Inst. Paris, **9**, 433 (1896).

³ Wied. Ann., **27**, 289 (1886).

⁴ Atti. di R. Ac. delle Sc. d. Torino, **20**, 607 (1885).

⁵ Loc. cit.

⁶ Z. physik. Chem., **6**, 524 (1890).

⁷ Ber. d. chem. Ges., **19**, 871 (1886).

⁸ Phil. Trans., **185A**, 307 (1894).

⁹ J. Chem. Soc., **51**, 360 (1897).

—21. The effect is shown in the following table, giving the “molecular viscosity at slope 0.0000323.”

Table I.

	Normal compound.		Iso-compound.	
	Found.	Calculated.	Found.	Calculated.
Pentane	687	689	663	668
Hexane	818	809	799	788
Heptane	931	929	908	908
Octane	1035	1049		

They found both maxima and minima when working with mixtures and, in the particular case of chloroform and ether, they found a point of inflection. They believe that the maximum value is caused by a “feeble chemical combination or molecular aggregation, which is destroyed by heat or dilution.”

It is to be expected that water and the alcohols would give abnormal results, since Ramsay and Shields¹ have shown that these liquids are associated. They are also abnormal in possessing a high dielectric constant.² Some of the characteristic properties of water, methyl alcohol, ethyl alcohol and acetone are grouped together below :

Table II.

	Mol. vol.	Viscosity.	Association.	Dielectric constant.
Water	18.0	0.01778	1.707	79.46
	at 0°	at 0°	at 0°	at 0°
	18.1	0.00891	1.644	73.92
Methyl alcohol	at 25°	at 25°	at 20°	at 20°
	39.5	0.0080846	2.65	34.05
	at 0°	at 0°	at -90°	
Ethyl alcohol	40.3	0.005530	2.32	
	at 20°	at 25°	at 20°	
	57.1	0.017761	2.03	25.02
Acetone	at 0°	at 0°	at -90°	
	58.3	0.0108545	1.65	
	at 20°	at 25°	at 20°	
Acetone	70.9	0.0039496	1.26	21.85
	at 0°	at 0°	at 17°-78°	
	73.2	0.0030726		
	at 20°	at 25°		

¹ Z. physik. Chem., **12**, 433 (1893) ; **15**, 111 (1894).

² *Ibid.*, **14**, 286 (1894).

No such quantitative relation has been worked out for changes in viscosity caused by salts brought into solution, and still less is known about the conductivity which a given salt may be expected to give. Yet Bredig,¹ Wagner² and Euler³ have worked on this problem with considerable success. Wagner found that the viscosity of a salt solution is an additive function of the metallic and non-metallic radicals of the dissolved salt. For allied metals the viscosity decreases as the atomic weight increases. The dissociated ions appear in some cases to have greater, and in other cases less viscosity than the original solution.

To explain this "negative viscosity" shown by certain salts in their power to lower the viscosity of pure water, Euler employed the "Electrostriction theory" proposed by Drude and Nernst.⁴ According to this theory the ion is surrounded by a strong electrical field, in virtue of its charge, which causes a strong compression of the liquid in this field. Euler holds that the effect of a salt on viscosity is the result of two tendencies; first, that of the atoms tending to increase the viscosity in inverse proportion to their migration velocities and, second, the electrostriction tending to lessen the viscosity.

Euler has calculated viscosity constants for a large number of ions and finds the relation between them and the migration velocities to be expressed by the formula

$$(A - 0.68).U(\text{or } (K - 0.68).V) = \text{a constant,}$$

where A and K are the viscosity constants and U and V are the migration velocities of the anion and cation, respectively. Hydrogen and hydroxyl ions are exceptions. Some of the values given are the following :

Table III.

Ion.	Migration velocity.	Viscosity constant.
Li	39.8	1.15
Ca	62.0	1.023
K	70.6	0.962
Br	73.0	0.946
NO ₃	..	0.919

¹ Z. physik. Chem., **13**, 243 (1894).

² *Ibid.*, **5**, 31 (1890).

³ *Ibid.*, **25**, 536 (1898).

⁴ *Ibid.*, **15**, 79 (1894).

Wagner¹ has shown that Mullenbein's² measurements have discounted Euler's explanation of negative viscosity, since the viscosity of the solvent may be lowered by the addition of certain non-electrolytes, even when the viscosity of the dissolved substance is higher than that of the solvent. With ethyl alcohol, *o*-nitrotoluene gives an inversion-point, *m*-nitrotoluene a minimum and *p*-nitrotoluene a maximum.

He proposes, as an explanation, that the solute diminishes the quantity of the solvent in a given space and this leads to a diminution of the viscosity, which diminution is partly compensated, however, by the solute itself. According to the relative magnitude of the various factors, the viscosity may be increased or diminished.

Dunstan³ has investigated a large number of mixtures. He believes that the increase in viscosity is due to the formation of loosely-held complexes. He thinks that the cause of the minimum of viscosity is more deep-seated than Wagner supposed and attributes it to "some change in molecular aggregation or dissociation."

Blanchard⁴ found that the addition of 1 equivalent of ammonia for 1 equivalent of silver, and the addition of 4 equivalents of ammonia for 1 equivalent of copper and zinc in aqueous solutions of their salts, very greatly decreases the viscosity. He reasons that this cannot be due to increased ionization, and therefore rejects the electrostriction theory and proposes a hydrate theory. He says that if the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot decrease its mass or readily increase its symmetry, so as to reduce the viscosity. The only explanation seems to be that the ions in solution are hydrated. The hydrate water is replaced by ammonia, which forms with the ion a more stable complex and one of smaller mass, or greater symmetry, or both. He believes that this theory also accounts for negative viscosity and for the effect of pressure on viscosity. Evidently, this is the same conclusion as that

¹ Z. physik. Chem., **46**, 867 (1903).

² Dissertation, Leipzig, 1901.

³ J. Chem. Soc., **85**, 817 (1904). Z. physik. Chem., **49**, 590 (1904).

⁴ J. Am. Chem. Soc., **26**, 1315 (1904).

reached by Kohlrausch in his hypothesis of ionic spheres, but by a somewhat different method of approach.

Blanchard added small amounts of water to alcoholic solutions of sodium hydroxide and found the viscosity smaller than would be expected from a study of the pure solvents. This is due, as he thinks, to the formation of a complex between the alkali, water and alcohol, which is, however, smaller or more symmetrical than the alcohol-water complex originally present.

Mixtures of alcohol and water give a maximum of viscosity. Blanchard finds that cupric chloride increases this effect. He further applies this theory to the work of Jones and Lindsay,¹ on conductivity.

The existence of hydrates or solvates (in the case of non-aqueous solvents) in one form or another is an old conception. Poisseuille² first suggested it in working with alcohol and water. Graham³ confirmed and extended Poisseuille's work. Wijkander⁴ supposed that acetic acid forms a hydrate with water, $C_2H_4O_2 \cdot H_2O$, which would account for abnormal viscosity. The changes due to temperature he attributed to dissociation changes in the liquid. Thorpe and Rodger⁵ and Traube⁶ also assume the presence of hydrates.

Recently, Varenne and Godefroy⁶ have found evidence from viscosity curves for the existence of various hydrates in mixtures of water with methyl and ethyl alcohols and acetone. These are as follows:

Table IV.

Methyl alcohol and water.	Ethyl alcohol and water.	Acetone and water.
$CH_3OH \cdot H_2O$	$C_2H_5OH \cdot 2H_2O$	$CH_3COCH_3 \cdot 3H_2O$
$CH_3OH \cdot 2H_2O$	$C_2H_5OH \cdot 3H_2O$	$CH_3COCH_3 \cdot 4H_2O$
$CH_3OH \cdot 3H_2O$	$C_2H_5OH \cdot 6H_2O$	$CH_3COCH_3 \cdot 8H_2O$
$CH_3OH \cdot 5H_2O$	$3(C_2H_5OH) \cdot 2H_2O$	$CH_3COCH_3 \cdot 34H_2O$
$CH_3OH \cdot 8H_2O$	$C_2H_5OH \cdot 22H_2O$	
$CH_3OH \cdot 20H_2O$		

¹ THIS JOURNAL, **28**, 329 (1902).

² *Loc. cit.*

³ Phil. Trans., **151**, 373 (1861).

⁴ Weid. Beibl., **8**, 3 (1879).

⁵ *Loc. cit.*

⁶ Compt. rend., **137**, 992 (1903); **138**, 990 (1904).

This conception of the existence of hydrates differs from the view put forward by Jones,¹ according to which the composition of the hydrates is simply a function of the concentration, the temperature remaining constant. The composition may vary all the way from 1 molecule of water to a large number, every intermediate step being represented. Various lines of evidence have been furnished for this view by Jones,² Jones and Getman,³ and Jones and Bassett.⁴ The more important of these have to do with the relation between water of crystallization and lowering of the freezing-point, certain color changes in solution and the relation between water of crystallization and temperature.

(c) *Conductivity*.—A great number of researches have been made on conductivity, using a large number of electrolytes and many different solvents. It is necessary to take up only that work which will help to bring out the relation between conductivity and viscosity.

In general, solvents that show abnormal conductivities when electrolytes are dissolved in them, have abnormal viscosities. Dutoit and Aston⁵ advanced the idea that dissociating power is related to the amount of polymerization of the solvent, as determined by the surface-tension method of Ramsay and Shields.⁶ On the other hand, Euler⁷ has shown that potassium iodide and various other salts give considerable conductivity in nitrobenzene and other non-associated or monomolecular solvents, while in butyric and valeric acids, which are highly associated, the conductivity is very small.

The facts as found by Euler support the hypothesis proposed by Thompson⁸ and Nernst,⁹ which attributes the dissociating power to the high dielectric constant of the medium ;

¹ THIS JOURNAL, **23**, 89 (1900).

² *Ibid.*, **23**, 89 (1900).

³ Z. physik. Chem., **46**, 244 (1903). THIS JOURNAL, **31**, 303 (1904). Z. physik. Chem., **49**, 385 (1904).

⁴ THIS JOURNAL, **33**, 584 (1905).

⁵ Compt. rend., **125**, 240 (1897).

⁶ Z. physik. Chem., **12**, 433 (1893); **15**, 111 (1894).

⁷ *Ibid.*, **28**, 619.

⁸ Phil. Mag., **36**, 320 (1893).

⁹ Z. physik. Chem., **13**, 531 (1894).

but Eversheim,¹ and Walden and Centnerzwer² have shown that, although liquid sulphur dioxide has a small dielectric constant, it gives a high conductivity. Therefore, both of these relations hold only approximately.

Plotnikow³ has shown that the dissociation is dependent somewhat upon the character of the dissolved substance, as well as upon the solvent. He obtained an abnormally great conductivity with the complex compound AlBr_3CS_2 in bromine solution, while most salts give little or none. He also obtained a maximum in molecular conductivity with PBr_5 dissolved in bromine, when the composition of the liquid corresponded to the formula $\text{PBr}_{2.5}$.

Zelinsky and Krapivin⁴ first noted a minimum in conductivity on mixing the solvents methyl alcohol and water. Cohen⁵ noted a minimum in dilute solutions of potassium iodide dissolved in mixtures of ethyl alcohol and water. Cohen remarked that either the dissociation in all the mixtures is the same or conductivity is not a measure of dissociation.

Jones and Lindsay⁶ worked with binary mixtures of methyl and ethyl alcohols and water. These alcohols and water gave a minimum at low temperatures, in most cases, and a 50 per cent mixture of methyl and ethyl alcohols gave a conductivity less than the mean value for the unmixed solvents. They proposed to account for this by assuming that each of the two associated solvents diminished the association of the other.

Jones and Carroll⁷ investigated the conductivity of sodium iodide, cadmium iodide, calcium nitrate and hydrochloric acid, in mixtures of methyl and ethyl alcohols and water. The minimum was observed in all cases at low temperatures. Recalling the hypotheses of Wiedemann, and of Dutoit and Friderich, connecting viscosity and conductivity, they proposed the quantitative relation

¹ *Ann. der Phys.*, **8**, 539 (1902).

² *Z. physik. Chem.*, **39**, 514 (1902).

³ *Ibid.*, **48**, 220 (1905).

⁴ *Ibid.*, **21**, 35 (1896).

⁵ *Ibid.*, **25**, 31 (1898).

⁶ *Loc. cit.*

⁷ *THIS JOURNAL*, **32**, 521 (1904).

$$\frac{\mu_v \eta}{x} = \text{constant} \quad \text{or} \quad \frac{\mu_v \eta}{\alpha} = \text{constant},$$

where x is the association factor and α the dissociation. These formulas become $\mu_v \eta = \text{constant}$ when $\mu_v = \mu \infty$.

This work has been continued and the relations between the viscosities and conductivities of lithium nitrate, potassium iodide and calcium nitrate, in various mixtures of acetone with methyl alcohol, ethyl alcohol and water have been worked out.

The work of Naumann,¹ on the solubility of salts in acetone, should also be mentioned.

(d) *Summary*.—An attempt will be made to sum up, in a brief paragraph, the factors that are already known to influence conductivity.

First, conductivity is dependent upon the number and velocity of the ions and only upon these factors, if we except the small conductivity of salts *per se*. The number of ions present is dependent upon the association factor or upon the dielectric constant of the solvent, and also upon the tendency of the atoms (or groups of atoms) to take up an electric charge, *i. e.*, more or less electro-positive or electro-negative.

The number of ions decreases with rise in temperature and with decreasing concentration. The velocity of the ions is dependent upon the fluidity of the solvent and upon the migration velocity of the ion itself. The fluidity of the solvent is, again, due to its association, to the concentration of the components having constitutive differences, and to the temperature. Pressure also affects the velocity of the ions.

Rise in temperature may decrease the association, or merely drive the molecules farther apart, giving a looser structure. The mobility of the ion is dependent upon its constitution and its affinity for the solvent, tending to produce an atmosphere of greater or less dimensions about itself.

We have not taken into account the result of the attractions between the charges on the ions, but it is not clear that the effect is measurable, and there is some doubt as to whether it is even in the direction indicated by Euler's hypothesis.

¹ Ber. d. chem. Ges., 37, 4328 (1904).

PART II.

EXPERIMENTAL.

Apparatus.

(a) *Conductivity*.—The Kohlrausch method of measuring conductivity, with Wheatstone bridge, telephone receiver and induction coil, was employed. It was not difficult to read to less than 0.1 of 1 per cent. The bridge wire was made of "manganin" and was calibrated before beginning the work. The resistance coils were standardized and found accurate to 0.04 of 1 per cent.

In order to work successfully with acetone, it was necessary to provide cells of special construction, so as to avoid the presence of rubber or wax,¹ which would be dissolved by the solutions. The cells were made of hard glass with ground-glass stoppers and had the form shown in Fig. I. The glass tubes

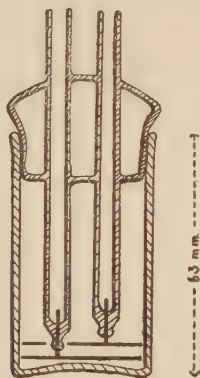


Fig. I.

carrying the electrodes were sealed into both the upper and the lower walls of the glass stopper. The distance between the electrodes thus remained permanently fixed.

The zero-bath was prepared by filling a large battery jar with clean, finely crushed ice, moistened with water. This was placed in a pail, made of compressed paper pulp and the annular space filled with finely crushed ice. Thus protected,

¹ Jones and Lindsay : *Loc. cit.*

the bath could be used for a much longer time than with the methods usually employed. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine. An Ostwald regulator was employed. The thermometers were regulated to tenths of a degree. They were tested at the beginning of the work. Burettes and flasks were carefully calibrated.

(b) *Viscosity*.—The viscometer was of the form recommended by Ostwald.¹ A fixed volume of the liquid to be measured was introduced into the apparatus. The liquid was raised exactly to the mark above the bulb, by air-pressure. The air was dried with sulphuric acid. The pressure was released by means of a Mohr pinch-cock, on a thick-walled rubber tube. By this arrangement the readings agreed to within 0.2 of a second. It was important that the liquids should be given time to drain out of the tube above the upper mark, since, otherwise, a drop of liquid might collect in the upper capillary and impede the entering air, thus introducing large error.

For the zero-bath a battery jar was filled with very finely crushed ice moistened with water. The ice was renewed as often as was necessary to keep the temperature constant. For the 25° bath a 5-liter beaker was employed. The bath was stirred by means of a hot-air engine, the temperature being kept to within 0°.1 of 25°, as in the conductivity method. The room was kept as near this temperature as possible.

We are indebted to Mr. Arthur C. Macy, jeweler, for the loan of a very accurate Waltham stop-watch, reading to two-tenths of a second.

To measure the specific gravities at zero, which was necessary in order to calculate the viscosities, we constructed a pycnometer, Fig. II. (p. 495), which would allow the large expansion of the alcohols and acetone and avoid loss by evaporation.

Preparation of Solutions.

In making up mixtures of solvents, n cc. of acetone diluted to 100 cc. was designated as a mixture of “ n per cent ace-

¹ *Physiko-chemische Messungen*, 2d Ed., p. 260.

tone." Since acetone, especially, has a high coefficient of expansion, it was important to have the temperature always the same, 20°. The acetone or alcohol was brought to this tem-

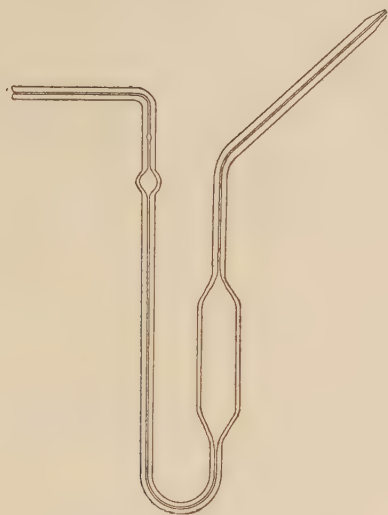


Fig. II.

perature before making up the mixture. On mixing acetone and water, contraction took place and heat was generated, so that the mixture was brought to the temperature before diluting to the mark.

The mother-solution was made by weighing into a measuring-flask the exact amount of salt required and adding the mixed solvent. Since, however, heat was again generated, especially with the calcium nitrate, the solution was again brought to the designated temperature before diluting to the mark.

From the mother-solution the other solutions were made by successive dilution. Where this would necessitate the use of small quantities of solution, a new mother-solution was made, and from this successive dilutions prepared.

Solvents.

Water.—The water was purified by the method of Jones and Mackay¹ and had a conductivity of 1×10^{-6} at 0° .

Methyl Alcohol.—The methyl alcohol was the best commercial article obtainable. It was boiled with calcium oxide for a day, distilled and allowed to stand over anhydrous copper sulphate for a long time. Before use it was distilled, using a Linnemann fractionating head. Precautions were taken against absorption of moisture. The first and last portions of the distillate were discarded, giving a liquid which boiled constantly at 66° . The mean value of the conductivity was 2×10^{-6} at 25° .

Ethyl Alcohol.—The ethyl alcohol was the best commercial alcohol obtainable. It was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 2×10^{-6} at 25° .

Acetone.—The acetone was dried over fused calcium chloride for weeks and distilled with a fractionating head as above. Its conductivity was 0.6×10^{-6} .

Conductivity Measurements.

In all determinations of conductivity at least three different resistances were used, and the values given are the mean. However, if the readings did not agree to 0.1 of 1 per cent, they were usually repeated. The constants of the cells were checked at frequent intervals. The cells were not allowed to remain in contact with the solution when not in use, nor to remain empty after being dried out with alcohol and ether. In the former case, small quantities of salt were found to be slowly absorbed and in the latter acetic acid was formed by the action of the platinum on the alcohol or ether in the presence of air. When not in use the cells were filled with pure distilled water.

A N/50 and a N/500 solution of potassium chloride were used in determining the cell constants. The conductivity of the former was taken as 129.7, at 25° . The value of the lat-

¹ Z. physik. Chem., **22**, 237 (1897). THIS JOURNAL, **19**, 91 (1897).

ter was determined several times in different cells. The mean value obtained agrees well with the interpolated values of other observers.

Table V.—Conductivity of *N/500 Potassium Chloride at 25°.*

Observed value corrected for the conductivity of water	136.5
Corresponding value obtained by Jones and West ¹	135.5
Deduced value, from Kohlrausch ²	136.94
Interpolated value, from Ostwald ³	138.7

The temperature coefficients are obtained by dividing the increase in the conductivity per degree, by the conductivity at the lower temperature.

Lithium Nitrate.

The lithium nitrate used in this work was a sample obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 150° until the weight remained constant. The salt was kept in a desiccator. The operation of drying was repeated whenever the salt was exposed to the air.

Table VI.—Conductivity of *Lithium Nitrate in Methyl Alcohol at 0° and 25°.*

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	31.17	43.05	0.0154
10	37.62	51.31	0.0145
25	43.40	60.49	0.0158
50	48.31	67.2	0.0157
100	52.0	72.6	0.0155
200	55.1	76.8	0.0147
400	56.8	80.0	0.0172
800	59.6	83.7	0.0162
1200	60.8	85.3	0.0160
1600	61.9	86.7	0.0160

¹ THIS JOURNAL, 34, 357 (1905).

² Leitvermögen der Elektrolyten.

³ Lehrbuch der allgemeinen Chem., 2d Ed., p. 732.

Table VII.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	33.50	44.27	0.0128
10	40.78	53.85	0.0128
25	48.36	64.63	0.0134
50	54.29	72.8	0.0136
100	58.9	79.8	0.0148
200	63.6	85.9	0.0140
400	66.2	90.6	0.0147
800	69.8	95.7	0.0148
1200	71.0	97.7	0.0150
1600	73.1	99.8	0.0146

Table VIII.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	32.79	41.26	0.0103
10	41.11	51.68	0.0100
25	51.38	65.39	0.0109
50	58.82	75.42	0.0113
100	65.2	84.8	0.0120
200	69.6	93.2	0.0135
400	75.2	99.2	0.0128
800	80.0	105.3	0.0127
1200	83.3	109.6	0.0126
1600	86.8	112.2	0.0117

Table IX.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	25.53	29.98	0.00703
10	34.06	39.45	0.0158
25	45.86	53.69	0.00683
50	55.50	66.30	0.0078
100	65.2	78.4	0.0081
200	74.8	92.2	0.0093
400	82.6	103.0	0.0099
800	90.0	113.3	0.0103
1200	94.4	119.0	0.0104
1600	96.6	123.6	0.0112

Table X.—Conductivity of Lithium Nitrate in Acetone at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	7.78	9.25	0.00755
10	9.67	10.87	0.00493
25	11.35	12.86	0.00532
50	14.07	15.64	0.00447
100	18.1	19.5	0.00310
200	23.8	25.3	0.00252
400	30.6	32.4	0.00232
800	43.4	45.5	0.00193
1200	48.7	52.5	0.00311
1600	55.3	59.8	0.00325

Table XI.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	31.17	33.50	32.79	25.53	7.78
10	37.62	40.78	41.11	34.06	9.67
25	43.40	48.36	51.38	45.86	11.35
50	48.31	54.29	58.82	55.50	14.07
100	52.0	58.9	65.2	65.2	18.1
200	55.1	63.6	69.6	74.8	23.8
400	56.8	66.2	75.2	82.6	30.6
800	59.6	69.8	80.0	90.0	43.4
1200	60.8	71.0	83.3	94.4	48.7
1600	61.9	73.1	86.8	96.6	55.3

Table XII.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	43.05	44.27	41.26	29.98	9.25
10	51.31	53.85	51.68	39.45	10.87
25	60.49	64.63	65.39	53.69	12.86
50	67.2	72.8	75.42	66.30	15.64
100	72.6	79.8	84.8	78.4	19.5
200	76.8	85.9	93.2	92.2	25.3
400	80.0	90.6	99.2	103.0	32.4
800	83.7	95.7	105.3	113.3	45.5
1200	85.3	97.7	109.6	119.0	52.5
1600	86.7	99.8	112.2	123.6	59.8

Table XIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent
5	0.0152	0.0129	0.0103	0.00703	0.00755
10	0.0145	0.0128	0.0100	0.00158	0.00493
25	0.0158	0.0134	0.0109	0.00683	0.00532
50	0.0157	0.0136	0.0113	0.0078	0.00447
100	0.0155	0.0148	0.0120	0.0081	0.00310
200	0.0147	0.0140	0.0135	0.0093	0.00252
400	0.0172	0.0147	0.0128	0.0099	0.00232
800	0.0162	0.0148	0.0127	0.0103	0.00192
1200	0.0160	0.0150	0.0126	0.0104	0.00311
1600	0.0160	0.0146	0.0117	0.0118	0.00325

Tables VI. to XIII. (Figs. III. and IV.) show that lithium nitrate, in mixtures of methyl alcohol and acetone, gives a pronounced maximum in conductivity. At high concentrations the maximum is rather small. As the dilution is in-

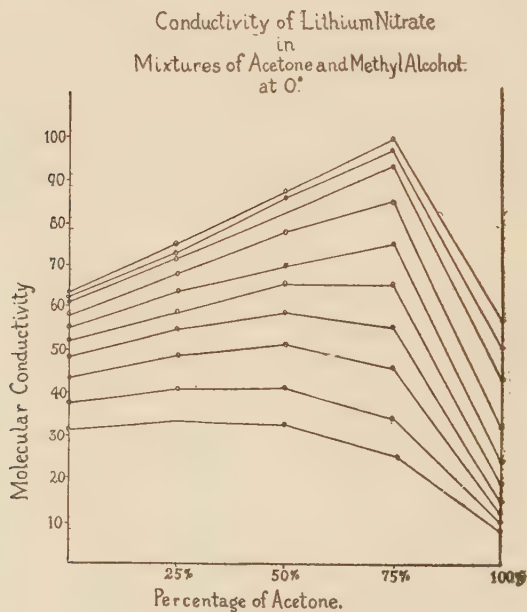


Fig. III.

creased the maximum appears in the 75 per cent mixture and even beyond. It should also be noticed that, in the dilute

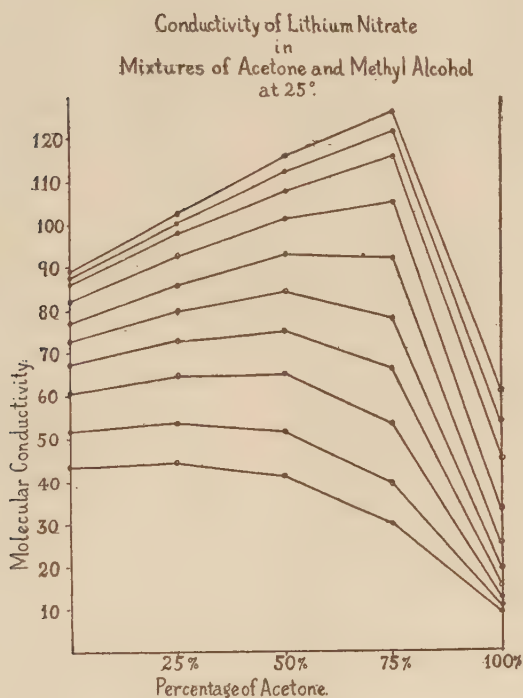


Fig. IV.

solutions, the rise in conductivity is directly proportional to the amount of acetone, up to the 75 per cent mixture. The maximum is increased by rise in temperature.

The points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.

Table XIV.—Conductivity of Lithium Nitrate in Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	9.14	14.65	0.0241
10	10.75	17.17	0.0238
25	13.55	21.71	0.0240
50	15.54	24.9	0.0241
100	16.9	27.6	0.0251
200	18.4	30.3	0.0260
400	19.1	32.1	0.0271
800	20.3	34.1	0.0251
1200	20.0	34.4	0.0288
1600	21.7	35.4	0.0252

Table XV.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	12.5	18.6	0.0195
10	15.9	22.9	0.0176
25	20.2	29.2	0.0178
50	23.1	33.9	0.0187
100	26.0	38.4	0.0191
200	29.0	43.2	0.0196
400	31.2	46.6	0.0198
800	33.0	50.3	0.0210
1200	34.6	51.8	0.0222
1600	35.1	54.5	0.0220

Table XVI.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	15.2	19.7	0.0142
10	19.6	25.4	0.0119
25	26.1	33.8	0.0118
50	30.9	40.4	0.0123
100	35.7	47.6	0.0133
200	40.4	54.8	0.0142
400	44.4	61.3	0.0152
800	47.4	67.0	0.0165
1200	49.4	69.6	0.0164
1600	50.7	71.9	0.0167

Table XVII.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.1	16.9	0.00795
10	19.3	22.5	0.0066
25	27.2	31.3	0.0060
50	34.3	39.7	0.0063
100	41.7	49.6	0.0074
200	50.2	60.1	0.0079
400	54.2	70.8	0.0122
800	64.9	80.9	0.0098
1200	69.5	86.5	0.0098
1600	70.6	91.7	0.0119

Table XVIII.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	9.14	12.5	15.2	14.1	7.78
10	10.75	15.9	19.6	19.3	9.67
25	13.55	20.2	26.1	27.2	11.35
50	15.54	23.1	30.9	34.3	14.07
100	16.9	26.0	35.7	41.7	18.1
200	18.4	29.0	40.4	50.2	23.8
400	19.1	31.2	44.4	54.2	30.6
800	20.3	33.0	47.4	64.9	43.4
1200	20.0	34.6	49.4	69.5	48.7
1600	21.7	35.1	50.7	70.6	55.3

Table XIX.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.65	18.6	19.7	16.9	9.25
10	17.17	22.9	25.4	22.5	10.87
25	21.71	29.2	33.8	31.3	12.86
50	24.90	33.9	40.4	39.7	15.64
100	27.60	38.4	47.6	49.6	19.5
200	30.3	43.2	54.8	60.1	25.3
400	32.1	46.6	61.3	70.8	32.4
800	34.1	50.3	67.0	80.9	45.5
1200	34.4	51.8	69.6	86.5	52.5
1600	35.4	54.5	71.9	91.7	59.8

Table XX.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol from 0° to 25° .

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0241	0.0195	0.0142	0.00795	0.00755
10	0.0238	0.0176	0.0119	0.0066	0.00493
25	0.0240	0.0178	0.0118	0.0060	0.00532
50	0.0241	0.0187	0.0123	0.0063	0.00447
100	0.0251	0.0191	0.0133	0.0074	0.00310
200	0.0260	0.0196	0.0142	0.0079	0.00252
400	0.0271	0.0198	0.0152	0.0122	0.00232
800	0.0251	0.0210	0.0165	0.00985	0.00192
1200	0.0288	0.0222	0.0164	0.0098	0.00311
1600	0.0252	0.0220	0.0167	0.0119	0.00325

Tables XIV. to XX. (Figs. V. and VI.) show the same characteristics for lithium nitrate, in mixtures of acetone and

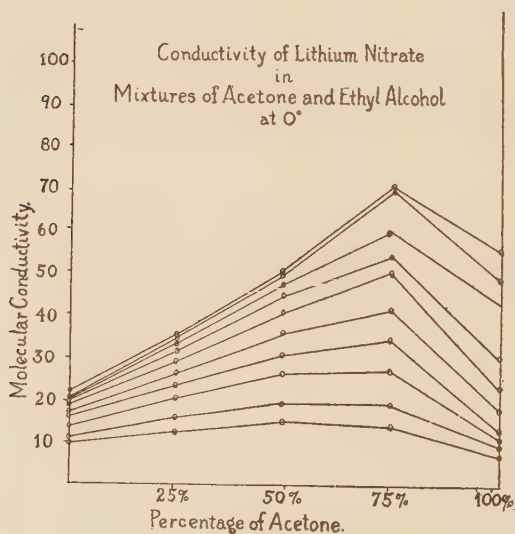


Fig. V.

ethyl alcohol, as those observed for the same salt in mixtures

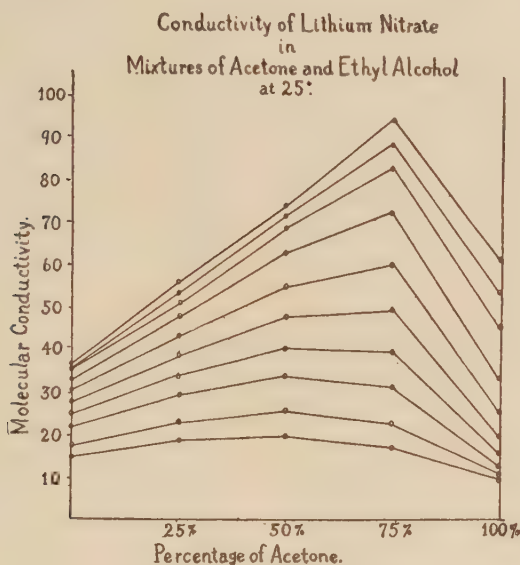


Fig. VI.

of acetone and methyl alcohol, but there is not such a well-defined maximum in these curves.

Table XXI.—Conductivity of Lithium Nitrate in Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	44.45	80.72	0.0323
10	46.39	83.87	0.0323
25	49.57	91.4	0.0334
50	51.4	94.4	0.0334
100	52.5	97.0	0.0340
200	53.1	98.8	0.0342
400	54.3	100.8	0.0341
800	55.0	102.0	0.0340
1200	55.9	102.6	0.0332
1600	56.3	102.8	0.0330
	(58.3)	(107.0)	

Table XXII.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.31	55.69	0.0415
10	27.37	56.35	0.0421
25	30.32	62.76	0.0427
50	31.50	65.3	0.0430
100	32.8	70.5	0.0460
200	34.1	72.5	0.0450
400	34.6	76.0	0.048
800	37.6	77.8	0.043
1200	39.0	80.7	0.0425
1600	40.0	83.1	0.0430

Table XXIII.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	21.81	43.37	0.0394
10	23.48	47.84	0.0415
25	24.90	51.33	0.0425
50	26.26	54.4	0.0427
100	27.2	57.3	0.0442
200	29.1	60.0	0.0425
400	28.8	60.0	0.0433
800	29.9	62.7	0.0440
1200	31.6	65.9	0.0425
1600	32.3	67.5	0.0435

Table XXIV.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	21.25	36.78	0.0292
10	24.41	42.65	0.0298
25	27.64	48.92	0.0308
50	30.25	54.14	0.0316
100	31.8	57.4	0.0322
200	33.5	61.4	0.0333
400	35.1	63.6	0.0325
800	36.7	66.3	0.0322
1200	38.1	68.6	0.0320
1600	37.8	69.1	0.0331

Table XXV.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	44.45	27.31	21.81	21.25	7.78
10	46.39	27.37	23.48	24.41	9.67
25	49.57	30.32	24.90	27.64	11.35
50	51.4	31.50	26.26	30.25	14.07
100	52.5	32.8	27.2	31.8	18.1
200	54.8	34.1	29.1	33.5	23.8
400	54.3	34.6	28.8	35.1	30.6
800	55.0	37.6	29.9	36.7	43.4
1200	55.9	39.0	31.6	38.1	48.7
1600	56.3	40.0	32.3	37.8	55.3

Table XXVI.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	80.72	55.69	43.37	36.78	9.25
10	83.87	56.35	47.84	42.65	10.87
25	91.4	62.74	51.33	48.92	12.86
50	94.4	65.3	54.4	54.14	15.64
100	97.0	70.5	57.3	57.4	19.5
200	98.8	72.5	60.0	61.4	25.3
400	100.8	76.0	60.0	63.6	32.4
800	102.0	77.8	62.7	66.3	45.5
1200	102.6	80.7	65.9	68.6	52.5
1600	102.8	83.1	67.5	69.1	59.8

Table XXVII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0323	0.0415	0.0394	0.0292	0.00755
10	0.0323	0.0423	0.0415	0.0298	0.00493
25	0.0334	0.0427	0.0425	0.0308	0.00532
50	0.0334	0.0430	0.0427	0.0316	0.00447
100	0.0340	0.0460	0.0442	0.0322	0.00310
200	0.0342	0.0450	0.0425	0.0333	0.00252
400	0.0341	0.048	0.0433	0.0325	0.00232
800	0.0340	0.043	0.0440	0.0322	0.00192
1200	0.0332	0.0425	0.0425	0.0320	0.00311
1600	0.0330	0.0430	0.0435	0.0331	0.00325

Tables XXI. to XXVII. (Figs. VII. and VIII.) for lithium

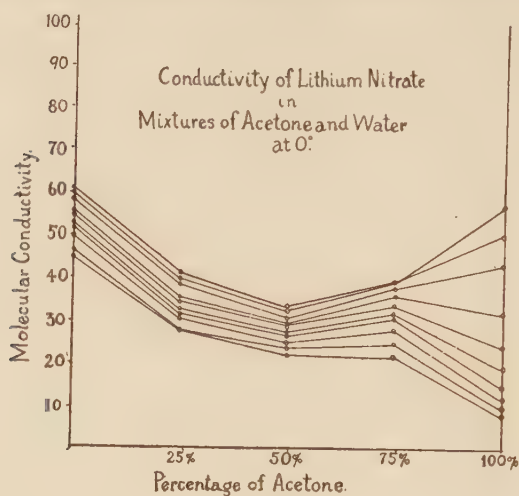


Fig. VII.

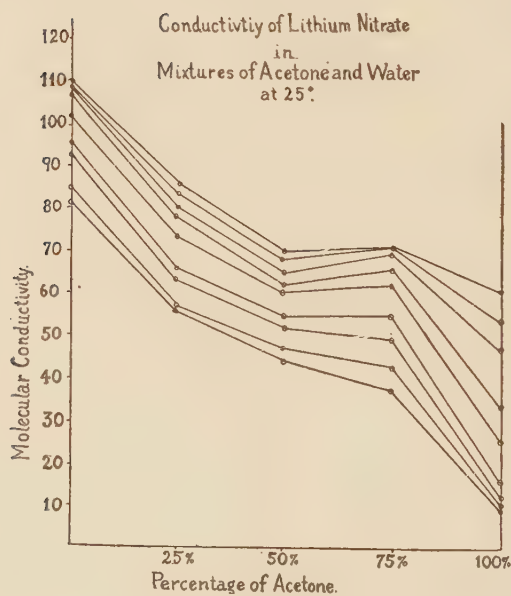


Fig. VIII.

nitrate, in mixtures of acetone and water show, at low temperatures and at high dilution, the minimum which is familiar under similar circumstances in mixtures of the alcohols and water. There is, however, even in this case, a tendency towards a maximum, which results in an inflection-point in most of the curves. It should be especially noticed that the curves diverge from each other rapidly, between the 75 per cent mixture and pure acetone. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

Potassium Iodide.

The salt gave no test for the presence of an iodate and the flame test showed no appreciable impurity. The salt was dried at 100° – 110° and kept in a desiccator. The salt dissolved in acetone, giving only a very slight coloration.

Table XXVIII.—Conductivity of Potassium Iodide in Methyl Alcohol at 0° and 25° .

<i>v.</i>	$\mu_v 0^{\circ}$.	$\mu_v 25^{\circ}$.	Temperature coefficients.
200	65.7	91.4	0.0156
300	68.1	94.6	0.0156
400	68.8	96.3	0.0159
600	70.1	99.0	0.0165
800	70.6	100.5	0.0169
1000	71.1	101.9	0.0174
1200	71.4	102.4	0.0174
1600	71.7	103.3	0.0176

Table XXIX.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25° .

<i>v.</i>	$\mu_v 0^{\circ}$.	$\mu_v 25^{\circ}$.	Temperature coefficients.
200	74.1	101.5	0.0148
300	75.6	103.7	0.0151
400	77.6	106.1	0.0147
600	78.1	108.8	0.0157
800	82.3	113.4	0.0151
1000	80.8	113.8	0.0163
1200	82.8	113.8	0.0149
1600	83.9	116.5	0.0155

Table XXX.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	82.7	110.3	0.0133
300	85.2	114.7	0.0139
400	87.2	114.8	0.0127
600	89.6	118.6	0.0129
800	91.9	121.8	0.0130
1000	93.6	123.1	0.0126
1200	93.7	126.2	0.0139
1600	94.1	129.2	0.0149

Table XXXI.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	93.1	117.0	0.0103
300	95.6	123.0	0.0115
400	97.8	124.3	0.0108
600	100.4	129.0	0.0110
800	104.1	131.8	0.0106
1000	103.7	132.7	0.0120
1200	104.3	135.7	0.0118
1600	106.5	137.7	0.0117

Table XXXII.—Conductivity of Potassium Iodide in Acetone at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	100.4	118.0	0.00701
300	105.8	126.2	0.00772
400	108.9	128.7	0.00730
600	112.3	134.1	0.00775
800	116.2	138.6	0.00772
1000	118.4	141.6	0.00785
1200	118.2	140.3	0.00750
1600	120.0	141.1	0.00704

Table XXXIII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	65.7	74.1	82.7	93.1	100.4
300	68.1	75.6	85.2	95.6	105.8
400	68.8	77.6	87.2	97.8	108.9
600	70.1	78.1	89.6	100.4	112.3
800	70.6	82.3	91.9	104.1	116.2
1000	71.1	80.8	93.6	103.7	118.4
1200	71.4	82.8	93.7	104.3	118.2
1600	71.7	83.9	94.1	106.5	120.0

Table XXXIV.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	91.4	101.5	110.3	117.0	118.0
300	94.6	103.7	114.7	123.0	126.2
400	96.3	106.1	114.8	124.3	128.7
600	99.0	108.8	118.6	129.0	134.1
800	100.5	113.4	121.8	131.8	138.6
1000	101.9	113.8	123.1	132.7	141.6
1200	102.4	113.8	126.2	135.7	140.3
1600	103.3	116.5	129.2	137.7	141.1

Table XXXV.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0156	0.0148	0.0133	0.0103	0.00701
300	0.0156	0.0151	0.0139	0.0115	0.00772
400	0.0159	0.0147	0.0127	0.0108	0.00730
600	0.0165	0.0157	0.0129	0.0110	0.00775
800	0.0169	0.0151	0.0130	0.0106	0.00772
1000	0.0173	0.0163	0.0126	0.0120	0.00785
1200	0.0174	0.0149	0.0159	0.0118	0.00750
1600	0.0176	0.0155	0.0149	0.0117	0.00704

Tables XXVIII. to XXXV. (Figs IX. and X.) for potassium iodide, in mixtures of acetone and methyl alcohol, show that the conductivity is almost exactly what we should expect

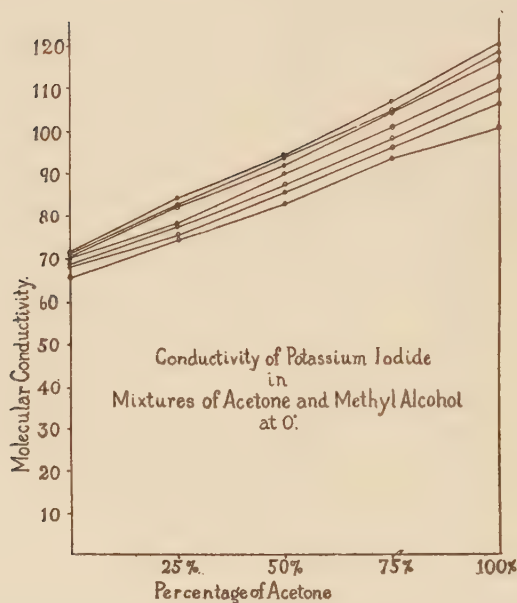


Fig. IX.

from the law of averages. There is, however, a slight tendency toward a maximum as we raise the temperature. In this respect the results are similar to those obtained with lithium nitrate. The values for the conductivity of potassium

iodide in pure water and in ethyl and methyl alcohols were taken from the work of Jones and Lindsay.

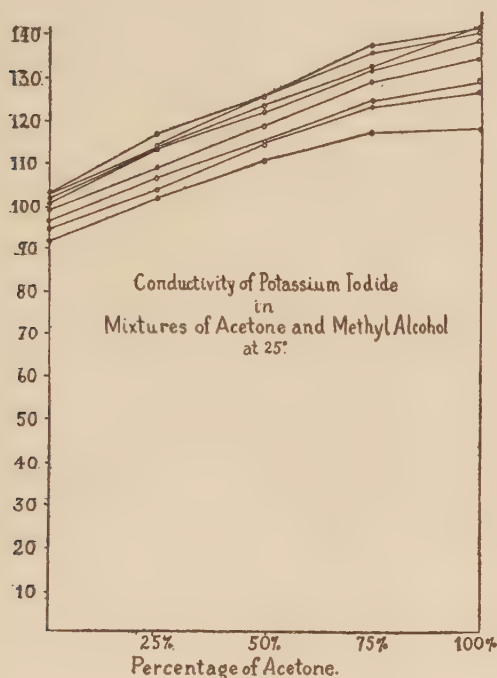


Fig. X.

Table XXXVI.—Conductivity of Potassium Iodide in Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	22.0	34.6	0.0230
300	23.2	36.5	0.0241
400	23.8	37.3	0.0238
600	25.5	39.1	0.0212
800	26.2	39.9	0.0209
1000	27.3	41.2	0.0202
1200	27.9	41.8	0.0200
1600	28.6	42.8	0.0194

Table XXXVII.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	35.5	52.5	0.0192
300	36.4	54.2	0.0196
400	37.8	56.3	0.0196
600	38.8	58.0	0.0197
800	40.3	60.5	0.0200
1000	39.8	59.7	0.0200
1200	39.7	60.8	0.0212
1600	40.1	63.5	0.0232

Table XXXVIII.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	52.2	71.4	0.0146
300	53.4	74.0	0.0155
400	56.1	76.8	0.0148
600	57.5	79.1	0.0150
800	59.5	82.6	0.0155
1000	59.7	82.9	0.0155
1200	59.8	82.9	0.0154
1600	61.3	85.4	0.0157

Table XXXIX.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	72.0	92.7	0.0115
300	75.3	97.5	0.0118
400	78.0	100.1	0.0113
600	79.5	102.4	0.0115
800	82.4	106.0	0.0114
1000	81.8	105.4	0.0115
1200	82.7	107.1	0.0118
1600	84.8	109.0	0.0114

Table XL.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	22.0	35.5	52.2	72.0	100.4
300	23.2	36.4	53.4	75.3	105.8
400	23.8	37.8	56.1	78.0	108.9
600	25.5	38.8	57.5	79.5	112.3
800	26.2	40.3	59.5	82.4	116.2
1000	27.3	39.8	59.7	81.8	118.4
1200	27.9	39.7	59.8	82.7	118.2
1600	28.6	40.1	61.3	84.8	120.0

Table XLI.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0° and 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	34.6	52.5	71.4	92.7	118.0
300	36.5	54.2	74.0	97.5	126.2
400	37.3	56.3	76.8	100.1	128.7
600	39.1	58.0	79.1	102.4	134.1
800	39.9	60.5	82.6	106.0	138.6
1000	41.2	59.7	82.9	105.4	141.6
1200	41.8	60.8	82.9	107.1	140.3
1600	42.8	63.5	85.4	109.0	141.1

Table XLII.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0230	0.0192	0.0146	0.0115	0.00701
300	0.0241	0.0196	0.0155	0.0118	0.00772
400	0.0238	0.0196	0.0148	0.0113	0.00730
600	0.0212	0.0197	0.0150	0.0115	0.00775
800	0.0209	0.0200	0.0155	0.0114	0.00772
1000	0.0202	0.0200	0.0155	0.0115	0.00785
1200	0.0200	0.0212	0.0154	0.0118	0.00750
1600	0.0194	0.0232	0.0157	0.0114	0.00704

Tables XXXVI. to XLII. (Figs. XI. and XII.) show the same characteristics for potassium iodide, in mixtures of acetone and ethyl alcohol, as those observed for the same salt in

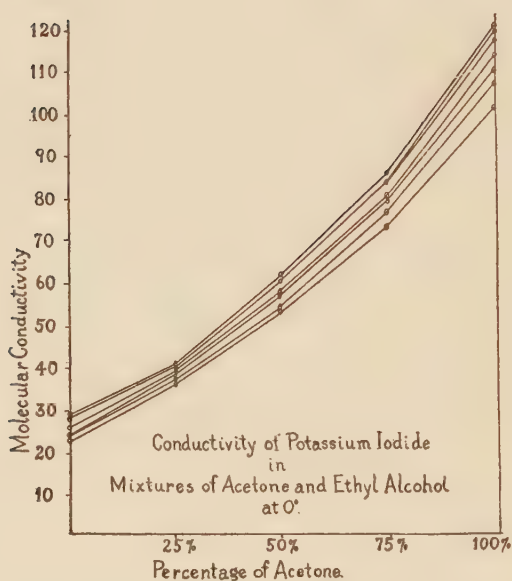


Fig. XI.

mixtures of acetone and methyl alcohol, but there is less of a tendency towards a maximum. In fact, there is a slight sagging in the curves. It is observed that this statement is

almost identical with the one in regard to lithium nitrate in mixtures of acetone and ethyl alcohol (p. 505).

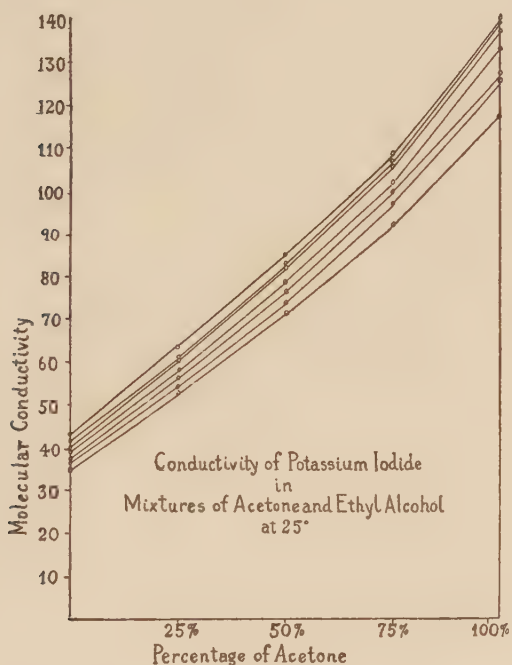


Fig. XII.

Table XLIII.—Conductivity of Potassium Iodide in Water at 0° and 25°.

<i>v</i> .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	76.7	136.3	0.0310
300	77.2	138.3	0.0316
400	77.5	138.8	0.0318
600	78.0	139.8	0.0312
800	78.0	140.1	0.0318
1000	78.0	140.6	0.0320
1200	78.0	140.7	0.0322
1600	78.0	140.7	0.0322

Table XLIV.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	44.6	91.1	0.0392
300	44.7	92.7	0.0430
400	45.3	92.4	0.0416
600	46.1	95.6	0.0430
800	47.0	96.9	0.0425
1000	46.3	96.2	0.0432
1200	47.5	102.9	0.0485
1600	47.8	100.1	0.0438

Table XLV.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	36.3	73.8	0.0413
300	36.8	75.9	0.0425
400	37.2	76.3	0.0420
600	37.6	77.7	0.0427
800	38.6	79.4	0.0423
1000	39.0	80.9	0.0430
1200	38.4	80.6	0.0439
1600	37.5	78.8	0.0440

Table XLVI.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	41.6	74.1	0.0311
300	41.9	74.1	0.0308
400	42.2	74.6	0.0304
600	42.8	75.4	0.0302
800	43.7	79.7	0.0330
1000	42.2	76.4	0.0320
1200	42.8	76.1	0.0310
1600	44.1	79.7	0.0321

Table XLVII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	76.7	44.6	36.3	41.6	100.4
300	77.2	44.7	36.8	41.9	105.8
400	77.5	45.3	37.2	42.2	108.9
600	78.0	46.1	37.6	42.8	112.3
800	78.0	47.0	38.6	43.7	116.2
1000	78.0	46.3	39.0	42.4	118.4
1200	78.0	47.5	38.4	42.8	118.2
1600	78.0	47.8	37.5	44.1	120.0

Table XLVIII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	136.3	91.1	73.8	74.1	118.0
300	138.3	92.7	75.9	74.1	126.2
400	138.8	92.4	76.3	74.6	128.7
600	139.8	95.6	77.7	75.4	134.1
800	140.1	96.9	79.4	79.7	138.6
1000	140.6	96.2	80.9	76.4	141.6
1200	140.7	102.9	80.6	76.1	140.3
1600	140.7	100.1	78.8	79.7	141.1

Table XLIX.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0310	0.0392	0.0413	0.0311	0.00701
300	0.0316	0.0430	0.0425	0.0308	0.00772
400	0.0318	0.0416	0.0420	0.0304	0.00730
600	0.0312	0.0430	0.0427	0.0302	0.00775
800	0.0318	0.0425	0.0423	0.0330	0.00772
1000	0.0320	0.0432	0.0430	0.0320	0.00785
1200	0.0322	0.0485	0.0439	0.0310	0.00750
1600	0.0322	0.0438	0.0440	0.0321	0.00704

Tables XLIII. to XLIX. (Figs. XIII. and XIV.) for potassium iodide, in mixtures of acetone and water, display a minimum in molecular conductivity. There is no tendency towards

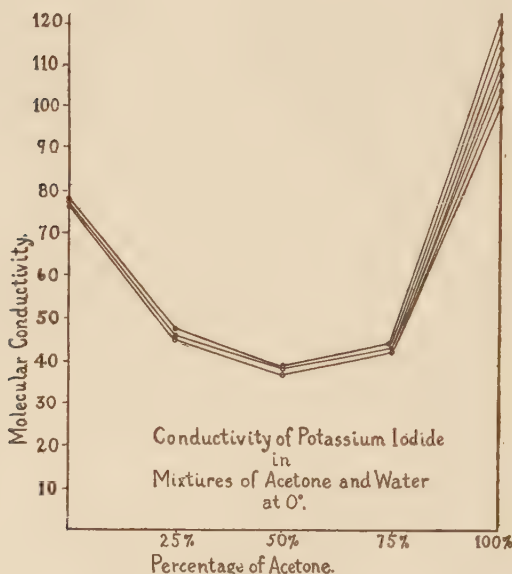


Fig. XIII.

a maximum. It should, however, be noticed that the divergence of the curves between the 75 per cent mixture and pure acetone is small. The salt is, therefore, quite largely dissociated at all dilutions in all of the mixtures.

It was thought advisable, at this stage, to use solutions of sodium iodide in the various mixtures. Solutions of sodium iodide in acetone had been investigated by Carrara,¹ Dutoit and Friderich² and by Jones.³ It was noticed, however, that

¹ Gazz. chim. ital., [1], 27, 207 (1897).

² Bull. Soc. Chim., [3], 19, 334 (1898).

³ THIS JOURNAL, 27, 16 (1902).

the solution had a high coloration, which deepened on standing. Moreover, there was a slight deposit formed at the same time. On evaporation the residue was still colored. The strongest solutions of the sodium iodide, in acetone, gave a

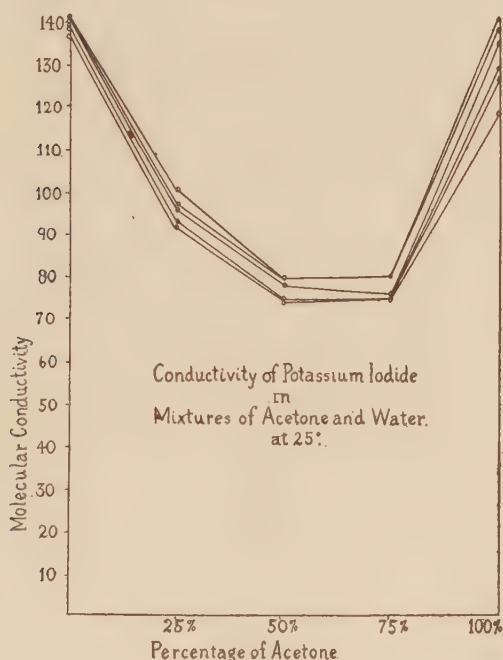


Fig. XIV.

test for iodine with starch paste, while the more dilute solutions, though still somewhat colored, gave none. Free iodine was then added to pure acetone until the same color was reproduced. This solution, tested with starch paste, gave no test for iodine. Time did not permit the further investigation of this interesting point.

Calcium Nitrate.

The calcium nitrate used was an anhydrous preparation obtained from Kahlbaum. It was heated for several days at

140°, until it had a constant weight. Subsequently, it was dried for some time at 140° after each exposure to the air. The salt then contained no calcium oxide, and showed no appreciable impurity by the flame test.

Table L.—Conductivity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 0°. (Carroll.)	μ_v 25°.	μ_v 25°. (Carroll.)	Temperature coefficients.
5	14.33		19.67		0.0149
10	18.98		25.38		0.0135
16				32.79	
25	27.66		36.77		0.0131
32		31.30		41.88	0.0135
50	34.6		45.7		0.0128
64		37.27		50.79	0.0145
100	42.2		55.9		0.0130
128		46.66		60.52	0.0119
200	49.9		65.4		0.0124
256		55.17		73.98	0.0136
400	58.2		75.6		0.0120
800	65.7		86.6		0.0127
1200	74.4		95.0		0.0111
1600	77.2		98.2		0.0109

Table LI.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	13.13	17.36	0.0129
10	17.76	23.08	0.0120
25	26.33	33.74	0.0111
50	33.9	43.2	0.0110
100	42.1	53.9	0.0112
200	50.7	66.8	0.0127
400	60.9	76.8	0.0105
800	71.0	89.4	0.0104
1200	79.7	98.0	0.0092
1600	82.6	102.7	0.0098

Table LII.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	10.16	12.97	0.0111
10	13.82	17.29	0.0100
25	21.30	26.11	0.00903
50	28.11	34.44	0.00895
100	35.7	42.8	0.00795
200	45.2	54.8	0.0085
400	55.3	68.3	0.0088
800	66.8	83.0	0.0097
1200	73.5	91.3	0.0097
1600	79.2	98.8	0.0099

Table LIII.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	6.07	7.65	0.0104
10	8.10	9.78	0.0083
25	12.40	14.56	0.0070
50	16.29	19.47	0.0078
100	21.65	25.1	0.00635
200	28.5	33.0	0.00630
400	38.1	44.3	0.0065
800	49.2	57.8	0.00698
1200	57.3	66.9	0.0067
1600	64.2	75.1	0.0068

Table LIV.—Conductivity of Calcium Nitrate in Acetone at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.93	4.96	0.0105
10	4.44	5.67	0.0111
25	5.06	6.55	0.0118
50	5.34	6.90	0.0117
100	5.48	7.06	0.0115
200	5.93	7.54	0.0109
400	6.69	8.22	0.00916
800	7.93	9.69	0.00884
1200	9.26	11.22	0.00847
1600	10.36	12.62	0.00873

Table LV.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.33	13.13	10.16	6.07	3.93
10	18.98	17.76	13.82	8.10	4.44
25	27.66	26.33	21.30	12.40	5.06
50	34.6	33.9	28.11	16.29	5.34
100	42.2	42.1	35.7	21.65	5.48
200	49.9	50.7	45.2	28.5	5.93
400	58.2	60.9	55.3	38.1	6.69
800	65.7	71.0	66.8	49.2	7.93
1200	74.4	79.7	73.5	57.3	9.26
1600	77.2	82.6	79.2	64.2	10.36

Table LVI.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	19.67	17.36	12.97	7.65	4.96
10	25.38	23.08	17.29	9.78	5.67
25	36.77	33.74	26.11	14.56	6.55
50	45.7	43.2	34.44	19.47	6.90
100	55.9	53.9	42.8	25.1	7.06
200	65.4	66.8	54.8	33.0	7.54
400	75.6	76.8	68.3	44.3	8.22
800	86.6	89.4	83.0	57.8	9.69
1200	95.0	98.0	91.3	66.9	11.22
1600	98.2	102.7	98.8	75.1	12.62

Table LVII.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0149	0.0129	0.0111	0.0104	0.0105
10	0.0135	0.0120	0.0100	0.0083	0.0111
25	0.0131	0.0111	0.00903	0.0070	0.0118
50	0.0128	0.0110	0.00895	0.0078	0.0117
100	0.0130	0.0112	0.00795	0.0063	0.0115
200	0.0124	0.0127	0.0085	0.0065	0.0109
400	0.0120	0.0105	0.0088	0.0065	0.00916
800	0.0127	0.0104	0.0097	0.00698	0.00884
1200	0.0111	0.0092	0.0097	0.0067	0.00847
1600	0.0109	0.0098	0.0099	0.0068	0.00873

Tables L. to LVII. (Figs. XV. and XVI.) for calcium nitrate, in mixtures of acetone and methyl alcohol, give a pronounced maximum in conductivity at high dilutions. It will

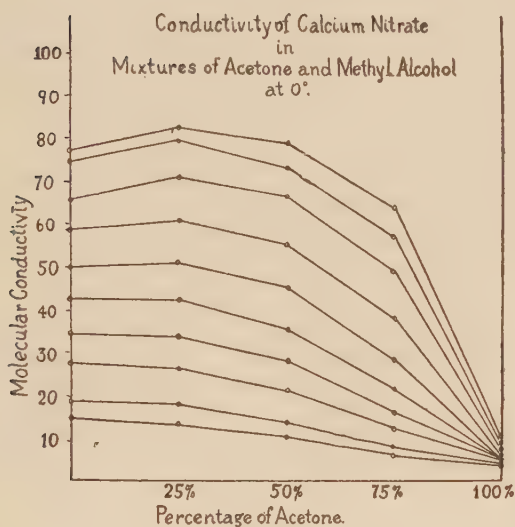


Fig. XV.

be recalled that Jones and Carroll obtained a minimum conductivity with this salt, in mixtures of ethyl alcohol and water, only at low temperatures and at high dilution. It should be noted that calcium nitrate is very slightly dissociated in acetone and that the maximum occurs in the 25 per cent mixture.

The temperature coefficients of conductivity decrease with the dilution, and they are also less in the mixtures than in the

pure solvents, the minimum appearing in the 75 per cent mixture.

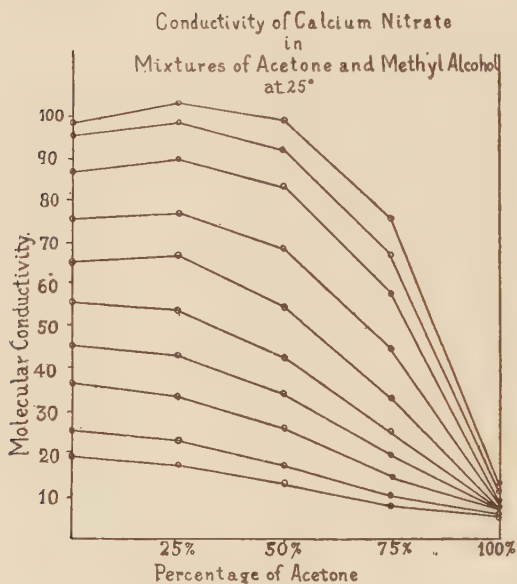


Fig. XVI.

Table LVIII.—Conductivity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.80	5.94	0.022
10	5.13	7.86	0.021
25	7.69	11.67	0.020
50	9.80	14.9	0.024
100	11.9	18.4	0.024
200	14.3	22.4	0.024
400	15.2	23.7	0.022
800	17.2	27.5	0.024
1200	18.1	29.5	0.024
1600	18.8	33.3	0.031

Table LIX.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	4.45	6.18	0.0156
10	6.01	8.29	0.0151
25	9.29	12.52	0.0140
50	12.20	16.59	0.0144
100	15.4	21.1	0.0148
400	22.3	32.2	0.0177
800	27.2	40.1	0.0190
1200	28.9	42.7	0.0191
1600	31.6	46.3	0.0186

Table LX.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	4.42	5.86	0.0130
10	6.00	7.64	0.0109
25	9.25	11.48	0.00963
50	12.33	15.24	0.00945
100	16.1	19.9	0.00942
200	20.7	26.0	0.0102
400	26.1	32.8	0.0102
800	31.8	41.4	0.0121
1200	35.8	46.8	0.0123
1600	38.0	50.7	0.0134

Table LXI.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.89	5.08	0.0123
10	4.80	5.99	0.00992
25	6.92	8.22	0.00753
50	9.20	11.34	0.00930
100	12.1	13.8	0.0056
200	16.2	18.3	0.0052
400	21.3	24.3	0.00562
800	28.1	32.7	0.0065
1200	33.2	39.1	0.0073
1600	36.2	42.4	0.0068

Table LXII.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	3.80	4.45	4.42	3.89	3.93
10	5.13	6.01	6.00	4.80	4.44
25	7.69	9.29	9.25	6.92	5.06
50	9.80	12.20	12.33	9.20	5.34
100	11.9	15.4	16.1	12.1	5.48
200	14.3	19.1	20.7	16.2	5.93
400	15.2	22.3	26.1	21.3	6.69
800	17.2	27.2	31.8	28.1	7.93
1200	18.1	28.9	35.8	33.2	9.26
1600	18.81	31.6	38.0	36.2	10.36

Table LXIII.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	5.94	6.18	5.86	5.08	4.96
10	7.86	8.29	7.64	5.99	5.67
25	11.67	12.52	11.48	8.22	6.55
50	14.91	16.59	15.24	11.34	6.90
100	18.4	21.1	19.9	13.8	7.06
200	22.4	26.5	26.0	18.3	7.54
400	23.7	32.2	32.8	24.3	8.22
800	27.5	40.1	41.4	32.7	9.69
1200	29.5	42.7	46.8	39.1	11.22
1600	33.3	46.3	50.7	42.4	12.62

Table LXIV.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.022	0.0156	0.0130	0.0123	0.0105
10	0.021	0.0151	0.0109	0.00992	0.0111
25	0.020	0.0140	0.00963	0.00753	0.0118
50	0.024	0.0144	0.00945	0.00930	0.0117
100	0.024	0.0148	0.00942	0.0056	0.0115
200	0.024	0.0155	0.0102	0.0052	0.0109
400	0.022	0.0177	0.0102	0.00562	0.00916
800	0.024	0.0190	0.0121	0.0065	0.00884
1200	0.024	0.0191	0.0123	0.0073	0.00847
1600	0.031	0.0186	0.0134	0.0068	0.00873

Tables LVIII. to LXIV. (Figs XVII. and XVIII.) for calcium nitrate, in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this

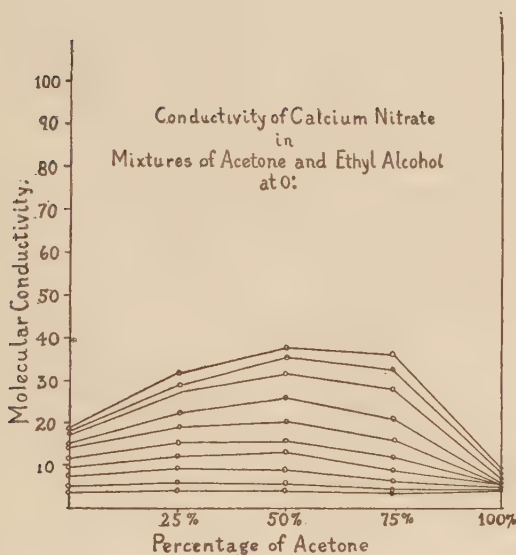


Fig. XVII.

salt in mixtures of acetone and methyl alcohol, but here the maximum is more prominent, being present at all dilutions and at both temperatures. The dissociation of calcium nitrate in ethyl alcohol, however, is small. With increasing dilution the maximum shifts from the 25 per cent mixture to the 75 per cent mixture.

The temperature coefficients in ethyl alcohol are almost constant, perhaps increasing slightly. The temperature coeffi-

cients of the mixtures show a minimum in the 75 per cent mixture. A similar phenomenon was noticed in the mixtures of acetone and methyl alcohol.

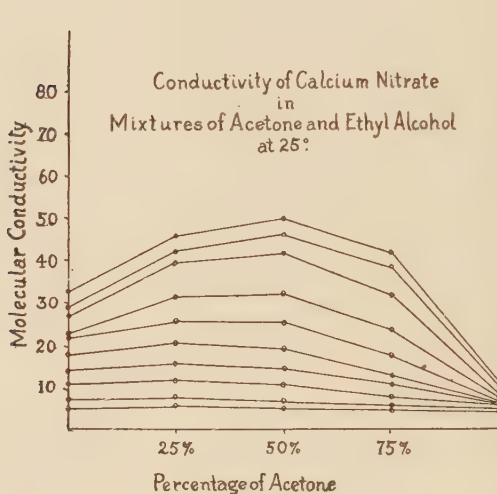


Fig. XVIII.

Table LXV.—Conductivity of Calcium Nitrate in Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	80.3	146.8	0.0331
10	89.8	165.5	0.0333
25	98.2	184.2	0.0350
50	107.0	192.2	0.0313
100	110.4	204.7	0.0341
200	114.9	214.2	0.0343
400	119.9	222.2	0.0341
800	123.4	232.2	0.0351
1200	...	238.5	..
1600	128.3	249.8	0.0378

Table LXVI.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	49.9	101.0	0.0410
10	55.0	112.3	0.0417
25	60.2	123.9	0.0423
50	64.8	134.0	0.0427
100	70.3	144.7	0.0423
200	72.3	154.1	0.0452
400	74.1	154.9	0.0441
800	76.8	161.0	0.0438
1200	79.1	165.4	0.0436
1600	80.0	167.7	0.0439

Table LXVII.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	36.9	73.4	0.0392
10	42.2	84.6	0.0402
25	46.7	94.8	0.0413
50	50.9	104.7	0.0423
100	54.8	115.4	0.0449
200	59.6	120.3	0.0458
400	61.4	128.0	0.0435
800	64.0	133.1	0.0433
1200	66.1	137.9	0.0434
1600	66.2	139.8	0.0444

Table LXVIII.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	25.0	43.1	0.0290
10	31.3	52.8	0.0272
25	40.1	68.3	0.0281
50	45.8	79.2	0.0291
100	52.6	92.3	0.0300
200	58.4	102.5	0.0301
400	62.6	114.9	0.0331
800	71.6	126.9	0.031
1200	75.1	133.5	0.031
1600	76.7	137.7	0.032

Table LXIX.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	80.3	49.9	36.9	25.0	3.93
10	89.8	55.0	42.2	31.3	4.44
25	98.2	60.2	46.7	40.1	5.06
50	107.0	64.8	50.9	45.8	5.34
100	110.4	70.3	54.8	52.6	5.48
200	114.9	72.3	59.6	58.4	5.93
400	119.9	74.1	61.4	62.6	6.69
800	123.4	76.8	64.0	71.6	7.93
1200	...	79.1	66.1	75.1	9.26
1600	128.3	80.0	66.2	76.7	10.4

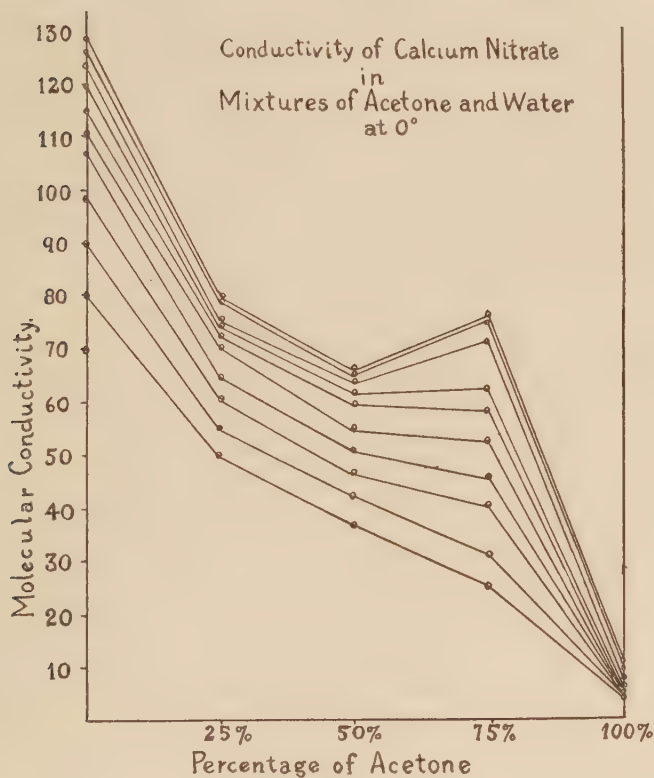
Table LXX.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	148.6	101.0	73.4	43.1	4.96
10	165.5	112.3	84.6	52.8	5.67
25	184.2	123.9	94.8	68.3	6.55
50	192.2	134.0	104.7	79.2	6.90
100	204.7	144.7	115.4	92.3	7.06
200	214.2	154.1	120.3	102.5	7.54
400	222.2	154.9	128.0	114.9	8.22
800	232.2	161.0	133.1	126.9	9.69
1200	238.5	165.4	137.9	133.5	11.2
1600	249.8	167.7	139.8	137.7	12.6

Table LXXI.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0331	0.0410	0.0392	0.0290	0.0105
10	0.0333	0.0417	0.0402	0.0272	0.0111
25	0.0350	0.0423	0.0413	0.0281	0.0118
50	0.0313	0.0427	0.0423	0.0291	0.0117
100	0.0341	0.0423	0.0449	0.0300	0.0115
200	0.0343	0.0452	0.0458	0.0301	0.0109
400	0.0341	0.0441	0.0435	0.0331	0.00916
800	0.0351	0.0438	0.0433	0.031	0.00884
1200	..	0.0436	0.0434	0.031	0.00847
1600	0.0378	0.0439	0.0444	0.032	0.00873

Tables LXV. to LXXI. (Figs. XIX. and XX.) for calcium nitrate, in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. In con-



centrated solutions, at high temperatures, the conductivity is what we should expect from the law of averages. These results are similar to those obtained with lithium nitrate in mixtures of acetone and water.

The temperature coefficients of conductivity of water increase with the dilution, while the temperature coefficients of acetone decrease with the dilution. In the 75 per cent mix-

ture the temperature coefficients are nearly independent of the dilution.

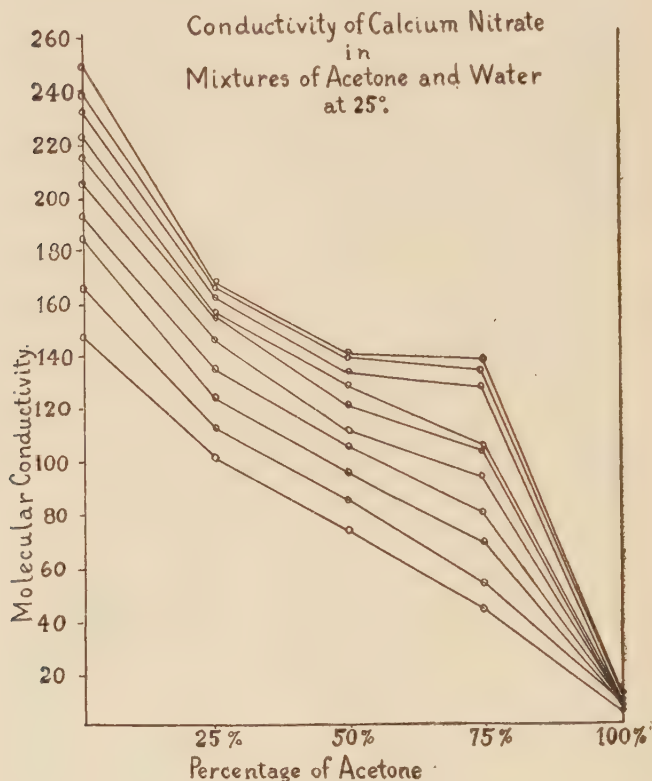


Fig. XX.

Viscosity Measurements.

In the following tables of viscosity data, the values of Thorpe and Rodger¹ for pure water, at 0° and 25°, are taken as the standard and the other values are referred to them; η represents viscosity, ϕ fluidity and D the density of the liquid in question, at 0° and 25°, compared with the density of water at 0° and 25°, respectively:

¹ Phil. Trans., 185A, 307 (1897.)

Table LXXII.—Fluidity of Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
Pure solvent	0.01778	56.24	1.000	0.00891	112.3	1.000	0.0426

Table LXXIII.—Fluidity of a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
Pure solvent	0.0293	34.12	0.9802	0.001276	78.37	0.9710	0.0518

Table LXXIV.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10							
1600				0.01397	71.59	0.948	
Pure solvent	0.03027	33.03	0.9522	0.0133	75.13	0.936	
				0.0133	74.96	0.937	0.0508

Table LXXV.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10							
1600				0.009617	104.0	0.892	
Pure solvent	0.0170	58.80	0.9023	0.009019	110.9	0.880	
				0.008904	112.3	0.879	0.0364

Table LXXVI.—Fluidity of Calcium Nitrate in Acetone at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.003544	282.1	0.803	
1600				0.003255	307.3	0.790	
Pure solvent	0.004097	244.1	0.8132	0.003237	308.9	0.788	0.0106

Table LXXVII.—Comparison of the Fluidities of Mixtures of Acetone and Water at 0°.

Pure solvent	0 per cent.	25 per cent.	50 per cent.	75 per cent.*	100 per cent.
	56.2	34.12	33.03	58.80	244.1

Table LXXVIII.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Water at 25°

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10			71.59	104.0	282.1
1600			75.13	110.9	307.3
Pure solvent	112.3	78.37	74.96	112.3	308.9

Table LXXIX.—Fluidity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.006179	161.8	0.804	
1600				0.005543	180.4	0.790	
Pure solvent	0.008185	122.2	0.811	0.005659	176.7	0.790	0.0178

Table LXXX.—Fluidity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.005319	188.0	0.811	
1600				0.004604	217.2	0.790	
Pure solvent	0.006498	153.9	0.816	0.004615	216.7	0.792	0.0163

Table LXXXI.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.004532	220.6	0.816	
1600				0.003926	254.7	0.794	
Pure solvent	0.005336	187.4	0.818	0.003891	257.0	0.794	0.0148

Table LXXXII.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.003909	255.8	0.812	
1600				0.003480	287.3	0.793	
Pure solvent	0.004501	222.2	0.817	0.003446	290.1	0.792	0.0122

Table LXXXIII.—Comparison of the Fluidities of Mixtures of Acetone and Methyl Alcohol at 0°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
122.2	153.9	187.4	222.2	244.1

Table LXXXIV.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	161.8	188.0	220.6	255.8	282.1
1600	180.4	217.2	254.7	287.3	307.3
Pure solvent	176.7	216.7	257.0	290.1	308.9

Table LXXXV.—Fluidity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5							
Pure solvent	0.01856	53.88	0.80820	0.01373	72.84	0.81612	0.0271
				0.01106	90.35	0.7895	

Table LXXXVI.—Fluidity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5							
Pure solvent	0.01041	96.08	0.81244	0.008444	118.4	0.81822	0.0220
				0.006714	148.9	0.791	

Table LXXXVII.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5							
Pure solvent	0.006801	147.0	0.81394	0.005861	170.6	0.81818	
				0.004874	205.2	0.7904	0.0148

Table LXXXVIII.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v .	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5							
Pure solvent	0.004990	200.4	0.81380	0.004484	223.0	0.81709	
				0.003776	264.8	0.7896	0.01296

Table LXXXIX.—Comparison of the Fluidities of Mixtures of Acetone and Ethyl Alcohol at 0°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
53.88	96.08	147.0	200.4	244.1

Table XC.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5					
Pure solvent	72.84	118.4	170.6	223.0	263.5
	90.35	148.9	205.2	264.8	308.9

Table XCI.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Water from 0° to 25° .

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0426	0.0518	0.0508	0.0364	0.0106

Table XCII.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Methyl Alcohol from 0° to 25° .

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0178	0.0163	0.0148	0.0122	0.0106

Table XCIII.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Ethyl Alcohol from 0° to 25° .

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0271	0.0220	0.0148	0.01296	0.0106

Tables LXXII. to XCIII. (Figs. XXI. and XXII.) show that

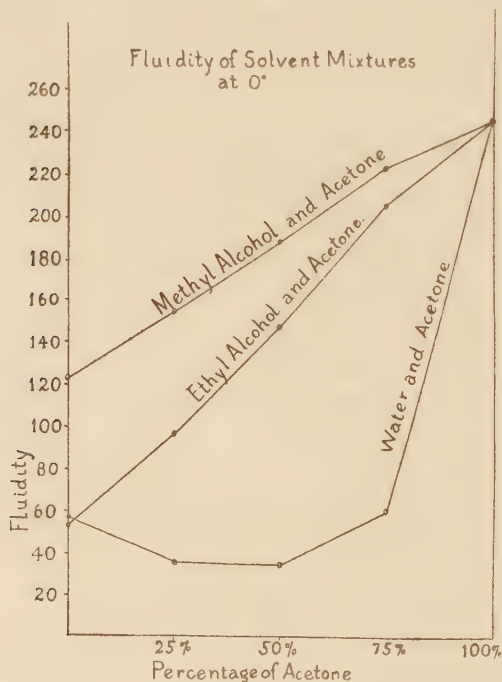


Fig. XXI.

there is a minimum of fluidity only in the case of acetone and water. In the mixtures of acetone with methyl alcohol we get somewhat larger values than would be expected from the

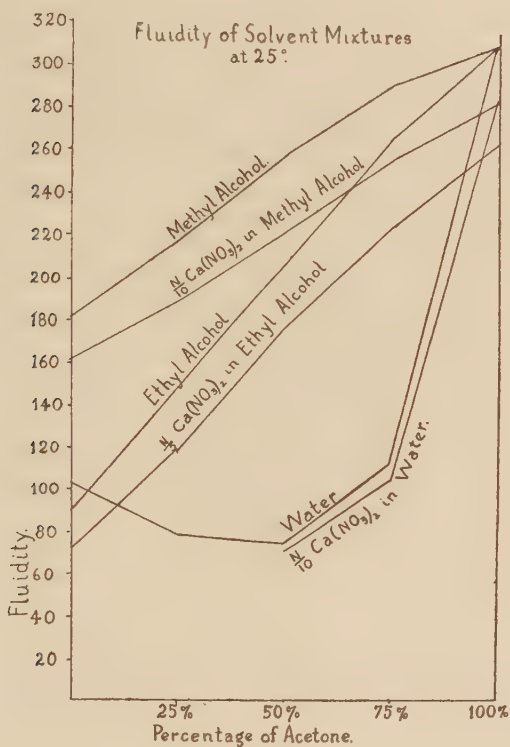


Fig. XXII.

fluidities of the pure solvents. This effect is not so apparent, however, in the case of acetone and ethyl alcohol. These last values were compared with those derived from Dunstan's results¹ and were found to be almost identical with them.

If we compare the viscosity curves of acetone and water with the fluidity curves, we find that the maximum is more pro-

¹ J. Chem. Soc., 85, 821 (1904).

nounced than the fluidity minimum. The viscosity curves for mixtures of acetone and the alcohols show a marked sagging, as Dunstan has pointed out.

Table XCIV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Water.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
<i>Fluidity:</i>						
Pure solv't . . .		0.0426	0.0518	0.0508	0.0364	0.0106
<i>Conductivity:</i>						
5	Ca(NO ₃) ₂	0.0331	0.0410	0.0392	0.0290	0.01050
1600	"	0.0378	0.0439	0.0444	0.0320	0.00873
5	LiNO ₃	0.0323	0.0415	0.0394	0.0292	0.00755
1600	"	0.0330	0.0430	0.0435	0.0331	0.00325
200	KI	0.0310	0.0392	0.0413	0.0311	0.00701
1600	"	0.0322	0.0438	0.0440	0.0321	0.00704

Table XCV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Ethyl Alcohol.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
<i>Fluidity:</i>						
Pure solv't . . .		0.0271	0.0220	0.0148	0.01296	0.0106
<i>Conductivity:</i>						
5	Ca(NO ₃) ₂	0.022	0.0156	0.0130	0.0123	0.0105
1600	"	0.031(?)	0.0186	0.0134	0.0068	0.00873
5	LiNO ₃	0.0241	0.0195	0.0142	0.00795	0.00755
1600	"	0.0252	0.0220	0.0167	0.0119	0.00325
200	KI	0.0230	0.0192	0.0146	0.0115	0.00701
1600	"	0.0194	0.0232	0.0157	0.0114	0.00704

Table XCVI.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Methyl Alcohol.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
<i>Fluidity:</i>						
Pure solv't	. . .	0.0178	0.0163	0.0148	0.0122	0.0106
<i>Conductivity:</i>						
5	Ca(NO ₃) ₂	0.0149	0.0129	0.0111	0.104	0.0105
1600	"	0.0109	0.0098	0.0099	0.0068	0.00873
5	LiNO ₃	0.0152	0.0129	0.0103	0.0104	0.00755
1600	"	0.0160	0.0146	0.0117	0.0112	0.00325
200	KI	0.0156	0.0148	0.0133	0.0103	0.00701
1600	"	0.0176	0.0155	0.0149	0.0117	0.00704

Tables XCIV. to XCVI. show that although the temperature coefficients of conductivity and fluidity vary in the same manner, yet the former are uniformly smaller than the latter.

Discussion of Experimental Results.

The curves for the conductivity of potassium iodide in all of the different mixtures, are very similar to the curves of fluidity in the corresponding mixtures. Lithium nitrate and calcium nitrate in all mixtures, at low temperatures, show a deviation from the fluidity curves, particularly in the 75 per cent mixtures, tending to produce a maximum in conductivity.

The work of Jones and Lindsay¹ and of Jones and Carroll¹ showed that solutions of lithium nitrate, in mixtures of methyl alcohol and water, gave curves with a simple minimum, like the fluidity curves for the corresponding mixtures. Calcium nitrate, dissolved in the same mixtures and also in mixtures of ethyl alcohol and water, in no case gave a minimum according to Jones and Carroll,¹ consequently, their curves are not similar to the corresponding fluidity curves.

Our results differ fundamentally from those heretofore observed, in that the mixtures of acetone with the alcohols and water show a tendency towards a maximum in the conductivity of solutions of certain salts, such as lithium nitrate and calcium nitrate.

¹ *Loc. cit.*

PART III.

Discussion of Results.

Since conductivity is dependent upon fluidity, and not *vice versa*, we will first discuss the fluidity curves and then the conductivity curves in connection with them.

When methyl alcohol or ethyl alcohol is mixed with acetone the fluidity curve of the mixtures is a straight line. This is what we should expect, if the fluidity of each of the components has its proportionate effect. Hence, we may conclude that the molecular aggregations of these pure solvents are not essentially changed in regard to size (or symmetry) by mixing the two solvents. We have already shown that the work of Thorpe and Rodger,¹ Traube,¹ Varenne and Godefroy¹ and others has made it evident that viscosity is dependent upon the character of the molecular aggregations present.

It may be objected that a straight line is not the "normal" fluidity curve, since, heretofore, a straight line has been considered to be the normal viscosity curve and the two conceptions are, in general, incompatible. To make this clear, let us suppose that we mix two liquids which are made up of particles which have no unusual action on each other, *i. e.*, do not form new aggregations of any kind. Two monomolecular liquids which do not form complexes on mixing would fulfil this condition. Further, let us suppose that the liquid is allowed to flow through a tube. The resulting fluidity would be the sum of the partial fluidities of the components. That is, the more rapidly moving particles would be held back by the slower ones, and the motion would be a mean value, proportional to the relative amounts of the components. Formulated this would be

$$(m_1 + m_2)\phi = m_1\phi_1 + m_2\phi_2 \dots \dots (1),$$

where m_1 and m_2 are the amounts of the components, and ϕ_1 and ϕ_2 are their respective fluidities.

This is similar to the conception which we have in electricity, where the conductance of two or more conductors is

¹ *Loc. cit.*

represented by the sum of their separate conductances. The conductance of a single conductor is expressed by the value

$$\frac{c \sigma}{l},$$

where c is the specific conductivity, σ the cross-section of the conductor and l the length. The conductance of a pair of conductors of different material, in parallel, is, per unit length,

$$(\sigma_1 + \sigma_2)c = c_1\sigma_1 + c_2\sigma_2.$$

Admitting this reasoning, it becomes evident that conductivity and fluidity are strictly comparable.

It will be noticed, moreover, that the *viscosities are not additive*.

If η_1 and η_2 represent the viscosities of the two components, then, since viscosity is the reciprocal of fluidity, we have from (1):

$$(m_1 + m_2) \frac{1}{H} = \frac{m_1}{\eta_1} + \frac{m_2}{\eta_2}.$$

By making m_1 and m_2 the percentages of the respective components:

$$\begin{aligned} \frac{1}{H} &= \frac{m_1}{\eta_1} + \frac{1 - m_1}{\eta_2} \\ \eta_1\eta_2 &= [m_1\eta_2 + (1 - m_1)\eta_1]H \\ &= [m_1(\eta_2 - \eta_1) + \eta_1]H \quad \dots \dots (2). \end{aligned}$$

Now let

$$m_1(\eta_2 - \eta_1) + \eta_1 = m'_1(\eta_2 - \eta_1)$$

then

$$m'_1 = m_1 + \frac{\eta_1}{\eta_2 - \eta_1}.$$

Substituting this value in (2),

$$m'_1 H = \frac{\eta_1 \eta_2}{\eta_2 - \eta_1} = \text{constant},$$

which is the equation of the equilateral hyperbola, the Y-axis of which is a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin, to which equation (1) is referred.

Thus, we seem justified in concluding that *the hyperbola is the normal curve for viscosities.*

From the above considerations we are led to the belief that inferences made from viscosity curves alone may lead to erroneous conclusions. For example, Wijkander¹ reached the conclusion that in no case is the viscosity identical with that calculated by the admixture rule. In the case of mixtures of ether with chloroform and of ether with carbon disulphide, there were inflection-points in the curves, but no simple relation between the viscosity coefficients of a mixture and those of its constituents could be deduced.

Linebarger² found that the observed viscosities, in general, were less than those calculated by the mixture rule, except, perhaps, in the case of mixtures of benzene and chloroform and mixtures of carbon disulphide and benzene, toluene, ether and acetic ether, where, according to Dunstan, the temperature of observation, 25°, was possibly too near the boiling-point of the carbon disulphide to make any specific influence which that liquid might exert at lower temperatures perceptible.

Dunstan³ makes the significant statement that "the law of mixtures is never accurately obeyed, and divergences seem to be more clearly marked in the case of viscosity than with other properties, such as refractive index."

These discrepancies are explained if our view be accepted, since the divergence in every abnormal case thus far investigated is smaller for the fluidity curves than for the corresponding viscosity curves, and the mixtures with carbon disulphide, which give "normal" viscosity curves, also give *fluidity* curves that are equally satisfactory. In the particular case of acetone and methyl alcohol or ethyl alcohol, the fluidity is a straight line, nearly to within the limits of experimental error,

¹ Weid. Beibl., 8, 3 (1879).

² Am. J. Sci., [4], 2, 331 (1896).

³ J. Chem. Soc., 85, 817 (1904). Z. physik. Chem., 49, 590 (1904).

so these two pairs of liquids may be considered as perfectly normal.

It must be stated explicitly that many of the conclusions of the above-mentioned workers are not changed by this new method of comparison of results, especially since, in many cases, they obtained curves with actual maxima and minima. These effects are reproduced in the fluidities as minima and maxima, respectively, which are generally less prominent than before.

A separate paper will be published in the near future, dealing with some of the recorded viscosity data from this new point of view.

When most of the organic solvents worked with up to this time are mixed with water, there is a very large increase in viscosity. In general, there is also a contraction on mixing these solvents and water. Some of those that give a pronounced maximum of viscosity are methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetic acid, propionic acid, butyric acid, isobutyric acid and acetone. The workers in this field have attributed the increase in viscosity to increase in the size of the molecular aggregations.

This decrease in fluidity retards the movement of the ions, hence there is a fall in molecular conductivity, which explains the minimum in conductivity heretofore observed by Zelinsky and Krapiwski,¹ Cohen,¹ Jones and Lindsay,¹ Jones and Carroll¹ and ourselves. This relation between viscosity and conductivity, as has been shown, has long been recognized. Wiedemann,¹ Stephan, Dutoit and Friderich and Jones and Carroll have been connected with the development of the exact relation between them.

If the salt happens to be highly dissociated in water and very little dissociated in the other solvent, the curves may be at such an angle with the axis of X that there will be only a sagging of the curve and not an actual minimum. Therefore, the *amount of deviation from the normal curve* appears to us to

¹ *Loc. cit.*

be a matter of prime importance, while the finding of a *minimum* is not.

If we could make a correction at the different parts of the curve for the different degrees of dissociation in the pure solvents and in the mixtures, we should then have a curve exactly parallel to the fluidity curve, if it is true that fluidity and dissociation are the only factors concerned, as Dutoit and Friderich and Jones and Carroll supposed. In our case it is almost impossible to make the correction with the data at hand, except, possibly, in the case of potassium iodide. The conductivity values for potassium iodide show that it is nearly dissociated in all mixtures, but with the other salts complete dissociation is not even approximately reached. Thinking that it might be possible to calculate μ_{∞} , we have tested Kohlrausch's formula,

$$\frac{\mu_{\infty} - \mu_v}{C^{1/3}} = K,$$

where C is the concentration and K is a constant. We found that it did not apply except in aqueous solutions. Völlmer¹ has already shown that the Ostwald dilution law does not apply to solutions in ethyl alcohol and methyl alcohol. Solutions of potassium iodide, in mixtures of methyl alcohol and water, were investigated by Zelinsky and Krapiwkin and Jones and Lindsay. The conductivity curves resemble the fluidity curves for methyl alcohol and water, as shown by Jones and Carroll. We have found the same similarity in the case of potassium iodide and water.

If we accept Kohlrausch's hypothesis of ionic spheres, it is evident that the atmosphere about the ions remains of the same size throughout all the mixtures; otherwise the ions would tend to show a maximum in conductivity in those mixtures where the atmosphere is smallest, causing a divergence from the fluidity curves. Difference in dissociation would also cause a divergence between the conductivity and fluidity curves. In the above case, however, the dissociation is large and all the curves are parallel.

¹ Ann. der Phys., **52**, 328 (1894).

If we pass now to potassium iodide in mixtures of acetone with methyl alcohol and ethyl alcohol, we find, again, that the conductivity curves and fluidity curves are very similar, *i. e.*, nearly straight lines, with a tendency towards a maximum, which is greater in the case of methyl alcohol than in that of ethyl alcohol. Evidently the changes in the size of the ionic spheres and the changes in the dissociation have either counteracted each other or remained zero.

Now let us consider lithium nitrate. In mixtures of acetone with the alcohols, we get a pronounced maximum in conductivity in the 75 per cent mixtures, at high dilutions. Since these solvents gave no such minimum in the case of potassium iodide, the maximum must be connected with the lithium nitrate itself. There are two possible explanations of the phenomenon: (1) Increase in dissociation in the 75 per cent mixture; (2) increase in the mobility of the ions, due to the diminution in the size of the ionic spheres. We shall attempt to decide between these two possibilities.

We have shown by consideration of the fluidities, that the liquids are not more associated in the mixtures than in the pure solvents, hence, if we accept the hypothesis of Dutoit and Aston, that dissociation power increases with the association of the solvent, the maximum cannot be due to increase in dissociation in the mixture. For example, calcium nitrate shows a pronounced maximum in conductivity in mixtures of alcohol and acetone, even though the dissociation of calcium nitrate in pure acetone is very small. It hardly seems probable that the acetone increases the dissociation of pure alcohol if it does not form complexes with it. We also have the fact, found by Jones and Carroll, that even in the case of alcohol and water, where molecular aggregations are known to be formed, there is not an increase in dissociation larger than the possible experimental error. Furthermore, if the 75 per cent mixture has the highest dissociating power, we should not expect to find the maximum migrating from the 25 per cent mixture to beyond the 75 per cent mixture, as the concentration of the dissolved substance decreases. This is the case with lithium nitrate, in mixtures of the alcohols and acetone. Finally, the

maximum in conductivity should manifest itself in the most concentrated solutions of potassium iodide, in mixtures of acetone with the alcohols. This is contrary to the facts. We, therefore, accept, tentatively, the view that *the maximum in conductivity is due, primarily, to a change in the dimensions of the ionic spheres.*

The determination, however, of the dissociation of lithium nitrate in pure alcohol, in pure acetone and in a 75 per cent mixture of these solvents, would be a very important check. Through the kindness of Mr. L. McMaster this point has been tested for acetone and ethyl alcohol, as shown in the table below :

Table XCVII.—Conductivity of Lithium Nitrate in Pure Acetone at 25°.

<i>v.</i>	μ_v 25° corrected.
2000	55.28
2500	62.87
3000	66.42

Table XCVIII.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 25°.

<i>v.</i>	μ_v 25° corrected.
2000	92.66
2500	100.55
3000	101.88

Table XCIX.—Conductivity of Lithium Nitrate in Pure Acetone at 25°.

<i>v.</i>	μ_v 25° corrected.
2000	37.01
2500	41.04
3000	41.48

The conductivity of the pure acetone used in these experiments was 1.516×10^{-6} ; that of the pure alcohol 0.857×10^{-6} .

These results show that complete dissociation is nearly reached only in the pure alcohol, and that the mixture is dissociated about as we might expect from the law of averages. We note that the maximum is very pronounced.

The conclusions of Dutoit and Friderich and of Jones and Carroll, that conductivity is inversely proportional to the viscosity and directly proportional to the association factor of the solvent (or to the amount of dissociation), are incomplete. It fails to take into consideration changes in the dimensions of the ionic spheres.

In the conductivities of lithium nitrate, in mixtures of acetone and water, the decreased fluidity manifests itself again. We notice, however, that the power of the acetone to produce smaller (or more symmetrical) ionic spheres is not destroyed by substituting water for methyl alcohol or ethyl alcohol. Practically all of the dilutions in the 75 per cent mixture of acetone and water show a decided elevation of the conductivity curves above those we should expect from similar measurements with potassium iodide. That increase in dissociation would make itself manifest in this way is doubtful, and our theory is thus strengthened.

Jones and Lindsay's results with lithium nitrate, in mixtures of water and methyl alcohol, do not show this effect, hence the acetone acts peculiarly in this respect. However, acetone behaves exceptionally in other ways.

At this point we should call attention to the fact that lithium forms a very slowly moving ion, *i. e.*, one with a large ionic sphere, while potassium forms a comparatively rapidly moving ion, *i. e.*, one with a small ionic sphere. The anions used do not differ greatly. Calcium forms an ion with a migration velocity between that of lithium and potassium. It was thought best to measure the conductivities of calcium nitrate in all of the mixtures, exactly as with the other salts.

The results show that the tendency towards a maximum in conductivity in the mixtures is very marked indeed. Moreover, they show that calcium nitrate is dissociated in the solvents very differently from lithium nitrate. Calcium nitrate is dissociated to a large extent in water and methyl alcohol, very much less in ethyl alcohol and still less in acetone. In spite of all differences, we are struck by the fact that the maximum *divergence* still tends to manifest itself in the 75 per cent mixture. Especially is this the case with acetone and water.

Let us now turn our attention to the concentrated solutions. In these we find the tendency towards a maximum very small, or entirely absent. If our explanation is correct, then, as the concentration of the salt increases, there will be less of the solvent for the formation of ionic spheres or, in the case of mixtures which tend to reduce the large atmospheres of the dilute solutions, the mass action of the solvent is much diminished.

Calcium nitrate is intermediate in its behavior between potassium iodide and lithium nitrate. It seems reasonable to connect this with the migration velocity. It would be interesting to experiment with sodium, the ion of which has a slow migration velocity, but, as we have shown, sodium iodide, although soluble, is unsuited for this purpose.

Summary.

We have measured the fluidities of mixtures of acetone with methyl alcohol, ethyl alcohol and water and of a few solutions of calcium nitrate in these mixtures.

We have measured the conductivity of various concentrations of lithium nitrate, potassium iodide and calcium nitrate, dissolved in the above mixtures.

These conductivities, in the case of mixtures of acetone and water, exhibit the minimum in conductivity previously observed by several other workers. Moreover, this minimum in conductivity has been shown to be intimately connected with the minimum in fluidity observed in these mixtures, but the conductivity curves of different salts show marked differences.

In the mixtures of acetone and the alcohols, the fluidities are what we should expect from the law of averages, *i. e.*, the fluidity curve is nearly a straight line. From this fact we have concluded that acetone and the alcohols thus far studied do not form more complex molecular aggregations when mixed than were originally present before mixing.

The conductivities of potassium iodide, in mixtures of acetone with methyl alcohol or ethyl alcohol, are also what we should expect from the law of averages—the conductivity curves are nearly straight lines at all dilutions. Again, the

conductivity has been shown to be intimately connected with fluidity.

Lithium nitrate and calcium nitrate, however, give a very pronounced *maximum in conductivity*, in mixtures of acetone with methyl alcohol or ethyl alcohol. Evidently this was an unexpected phenomenon; to explain it all of the factors that could reasonably influence conductivity were collected. After the elimination of several of them, the possible explanations were shown to be either in an increase in dissociation, giving rise to more ions, or in a diminution in the size of the ionic spheres already in the solution.

It was then shown to be possible to eliminate one of these factors by the following considerations:

1. The fluidity of the mixtures of acetone and alcohol shows that there is no increase in molecular aggregation, hence, we should not expect increased dissociation, if we accept the hypothesis of Dutoit and Aston.

2. Jones and Carroll have shown that, even in the case of alcohol and water, there is practically no increase in dissociation in the mixtures.

3. Furthermore, the maximum migrates from the 25 per cent mixture, at high concentration, to the 75 per cent mixture in the more dilute solutions. This would hardly be expected if the dissociating power is greatest in a certain mixture.

4. Potassium iodide shows no tendency towards a maximum of conductivity in the most concentrated solution with which we worked.

5. Very recent measurements, at extreme dilution, have failed to show any great difference in the dissociating power of the mixtures from that of the pure solvents.

We, therefore, seemed justified in the conclusion that the maximum in conductivity is due to a change in the dimensions of the atmospheres about the ions.

The conclusion of Dutoit and Friderich and of Jones and Carroll, that conductivity is proportional to the dissociation, and inversely proportional to the viscosity, has been shown to be incomplete in not taking into consideration possible changes in the size of the ionic spheres.

The conductivities of lithium nitrate and calcium nitrate, in mixtures of acetone and water, again show a tendency towards a maximum, in spite of the great diminution in fluidity.

Finally, it has been pointed out that the tendency to form a maximum in conductivity increases from potassium iodide, through calcium nitrate, to lithium nitrate, which seems to show these effects most strongly. This may be connected with the migration velocities of these ions.

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